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THE KINETICS OF NITRIC OXIDE FORMATION
IN HIGH PRESSURE COMBUSTION PROCESSES

Syed M. Shahed

Wisconsin University

Prepared for:

Public Health Service

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**Prepared for
Office of Research Grants
National Air Pollution Control Administration
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**The University of Wisconsin
Department of Mechanical Engineering
Madison, Wisconsin**

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TECHNICAL REPORT

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THE KINETICS OF NITRIC OXIDE FORMATION
IN HIGH PRESSURE COMBUSTION PROCESSES

Syed Mohammed Shahed

Under the supervision of

Associate Professor Henry K. Newhall

Nitric Oxide is recognized as one of the major combustion related air pollutants. For this reason it is desirable to understand as completely as possible the kinetics of nitric oxide formation in practical combustion processes.

The purpose of this work has been experimental measurement of the rate of formation of nitric oxide in combustion processes occurring under conditions similar to those found in practice. At the same time, development of a reaction mechanism and chemical kinetic calculation technique capable of accurately predicting formation rates of nitric oxide has been attempted.

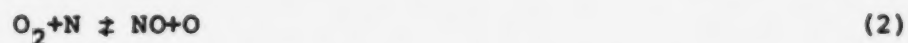
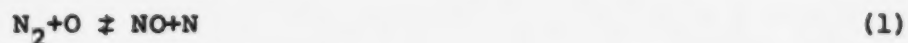
Ultraviolet absorption techniques were used to directly record the time rate of formation of nitric oxide in the immediate vicinity of a flame front propagating through a high pressure combustion vessel. Combustion pressures existing during measurements ranged from 20 to 30 atmospheres with calculated temperature ranging from 2500 to 3000°K.

Hydrogen and propane were used as fuels. The oxidizer was air or air diluted with nitrogen. Hydrogen was selected because of the relatively well known combustion kinetics of

hydrogen-air mixtures. Propane was chosen as a vapor state fuel representative of the straight chain hydrocarbons. A wide range of fuel-air ratios was studied. Further, experiments were carried out using hydrogen-air-diluent mixtures in order to study the effects of fuel-air ratio and combustion temperature independently.

Experimental measurements yielded values of nitric oxide concentration as a function of time during the combustion process. Flame position relative to the point of nitric oxide measurement was recorded simultaneously with nitric oxide concentration. On the basis of these measurements it was concluded that nitric oxide formation is a post-flame phenomenon occurring after combustion of the fuel has been substantially completed.

From a survey of the published literature a large number of elementary chemical reactions relevant to the formation of nitric oxide were tabulated. Published rate constants for these reactions were used in a machine calculation to predict the rate of formation of nitric oxide in post-flame gases. The relative contributions of the many elementary chemical reactions considered were examined and it was concluded that the following two elementary chemical reactions are sufficient to accurately predict the rate of formation of nitric oxide.



Making use of the above reactions a first order non-linear differential equation is obtained. The solution of this

$$\frac{d[\text{NO}]}{dt} = k_{1f}^{(T)} [\text{N}_2] [\text{O}] + k_{2f}^{(T)} [\text{O}] [\text{N}] - k_{1b}^{(T)} [\text{NO}] [\text{N}] - k_{2b}^{(T)} [\text{NO}] [\text{O}]$$

equation gives the concentration of nitric oxide as a function of time. Such a solution requires a knowledge of the temperature of burnt gases for evaluation of rate constants and the concentrations of atomic and molecular oxygen and nitrogen. The time for relaxation of these species to their respective chemical equilibrium concentrations in post-flame gases was estimated and found to be several orders of magnitude less than the measured times of nitric oxide formation. It was therefore concluded that chemical equilibrium concentrations of O_2 , N_2 , O and N can be employed in the solution of the rate equation. Adiabatic flame temperatures were calculated and used in the solution. A computer program was developed for the stepwise integration of the rate equation. Experimentally measured pressure-time histories were used to calculate the shifting equilibrium concentrations of atomic and molecular oxygen and nitrogen together with adiabatic flame temperatures. Use of these values in the integration of the rate equations gave concentrations of nitric oxide as a function of time. Calculated results compare very well with experimentally measured values.

The following major conclusions are derived from the present work:

X

1. Nitric oxide formation in hydrogen-air and hydrocarbon-air combustion processes is a post-flame phenomenon occurring only after combustion of the fuel is substantially complete.

2. The rate of formation of nitric oxide in such combustion processes is accurately predicted by the stated simple reaction mechanism used in conjunction with chemical equilibrium concentrations of atomic and molecular oxygen and nitrogen.

Henry K. Newhall
10/2/70

CHAPTER I INTRODUCTION

1.1 Literature Survey

It is presently recognised that oxides of nitrogen are serious air pollutants and are a necessary ingredient for the formation of photochemical smog (32,43). In the United States automobile engines form the largest single source of atmospheric nitrogen oxides, contributing more than fifty percent of the total emitted (1). Campau and Neerman (5) have demonstrated through the use of mass spectroscopic techniques, that the principal oxide of nitrogen present in the exhaust of such engines is nitric oxide, NO, forming 99 percent of the total oxides of nitrogen emitted.

For this reason the emission of nitric oxide from automotive engines has been the subject of fairly intensive study over the past 10-15 years. A great bulk of such work has been the study of the effect of engine operating variables on exhaust concentrations of nitric oxide. Some of the more commonly studied engine variables are air-fuel ratio, ignition timing, coolant temperature, manifold vacuum, exhaust back pressure, valve overlap and engine load etc. -- Huls and Nickol (21), Spindt et al (47), Deeter et al (6), Campau and Neerman (5), Alperstein and Bradow (3) and many others.

Such studies while quite valuable in themselves, do

not yield basic knowledge of the formation mechanism of nitric oxide. No quantitative conclusions concerning the rate of nitric oxide formation nor the elementary reactions responsible for its formation can be drawn from the results of such work. The few attempts at studying the formation rates of nitric oxide in internal combustion engines have involved extraction and subsequent chemical analysis of gas samples from the combustion chamber and exhaust (3,51). Such measuring techniques have two major limitations. Firstly, it is questionable if the small sample withdrawn is representative of the bulk combustion gases and secondly, there is the possibility of chemical reaction continuing to take place in the withdrawn sample.

Alperstein and Bradow (3) and Wimmer and McReynolds (51) describe some of the refined sampling techniques used. They conclude that the concentration of nitric oxide appearing in the exhaust of automobile engines tends to approach equilibrium concentrations for peak combustion temperatures rather than measured exhaust temperatures. It is argued that during combustion nitric oxide is formed rapidly reaching near equilibrium values corresponding to peak combustion temperatures and pressures and thereafter its concentration remains fixed or frozen at this level due to the rapid cooling of the expanding mixture of burnt gases.

The freezing of nitric oxide during expansion has been exhaustively studied by Newhall (38,39,40) and Starkman

(48). In these studies direct infrared spectroscopic techniques have been used to measure the concentration of nitric oxide during the expansion stroke of an internal combustion engine. Along with experimental measurements theoretical, chemical kinetic calculations have been carried out to predict the freezing of nitric oxide during expansion. As a result of such studies a fair understanding of the decomposition kinetics of nitric oxide during expansion is presently available. Relatively little, however, is known of the formation kinetics of nitric oxide during and after combustion.

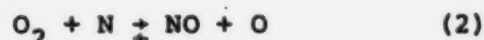
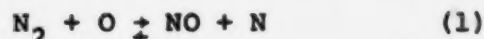
Further, in measurements made by Newhall (38) and by Wimmer and McReynolds (51) some discrepancy exists between measured exhaust concentrations of nitric oxide and equilibrium concentrations corresponding to peak combustion temperatures, the measured values being somewhat less than the equilibrium values. This discrepancy has been attributed variously to three factors -- one - partial decomposition of nitric oxide during the early part of expansion, two - an imperfect knowledge of combustion temperatures and three - a lagging equilibration of nitric oxide during formation.

It is thus apparent that a fairly detailed parametric study of the effect of engine operating variables on exhaust concentrations of nitric oxide has been carried out. The decomposition mechanism of nitric oxide is also fairly

well understood. Some of the qualitative conclusions that can be drawn from the results of parametric studies are that the formation of nitric oxide is sensitive to temperature and available concentrations of oxygen. Making use of these conclusions attempts have been made to reduce the exhaust concentrations of nitric oxide by reducing peak combustion temperatures. Deeter et al (6) and Daigh and Deeter (7) and Kopa and Kimura (29) have studied experimentally and theoretically the effect of diluting the charge with recirculated exhaust products. Newhall (37) has carried out a detailed theoretical study of the effect of the amount and temperature of recirculated exhaust on peak combustion temperatures and corresponding equilibrium concentrations of nitric oxide. The effect of recirculation on engine power is also considered. Nicholls et al (41) have studied experimentally and theoretically the effects of inlet manifold water injection on exhaust concentrations of nitric oxide.

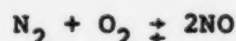
The mechanism of nitric oxide formation has received considerably less attention by comparison. An early and important work by Zeldovich and co-workers (53,54) is now available in an English translation. The conclusions arrived at in the present work are in very close agreement with those of Zeldovich in so far as such comparison is valid. The mechanism of formation of nitric oxide suggested

by them is sometimes known in the literature as the Zeldovich mechanism.



This same mechanism has been considered in the present work.

An alternate mechanism has been used by Eyzat and Guibet (8).



They have used this mechanism in conjunction with experimentally measured combustion process pressure time histories to attempt prediction of the formation of nitric oxide. However, the comparison of experimental and theoretical work involves a comparison of calculated and measured exhaust concentrations of nitric oxide rather than of the concentration time history of nitric oxide. Further, the mechanism used fails to predict concentrations of nitric oxide in the exhaust. A more recent work of Lavoie et al (33) uses the Zeldovich mechanism in addition to four other reactions involving N_2O and OH .

1.2 Purpose and Scope of This Work.

It is apparent from a review of literature that while an extensive parametric study of exhaust concentrations of nitric oxide as related to engine operating variables has been carried out and while a fair experimental and theo-

retical understanding of the decomposition of nitric oxide exists, little is known at the present time of the mechanism of formation of nitric oxide in flames.

In view of the current lack of understanding of nitric oxide formation and in view of the particular sparsity of time resolved experimental data, a program of study has been undertaken with the object of investigating in detail the chemical kinetic mechanism of formation of nitric oxide under conditions physically similar to those occurring in an internal combustion engine. The study has involved experimental and theoretical investigation of the rate of formation of nitric oxide.

Spectroscopic techniques have been used to directly measure and record the time rate of formation of nitric oxide in the immediate vicinity of a flame front propagating through a high pressure combustion vessel of fixed volume. A high degree of time and space resolution has been achieved.

Hydrogen-air, propane-air and hydrogen-air-diluent reactant mixtures have been studied where nitrogen has been used as a diluent.

A theoretical study has been carried out to predict the formation of nitric oxide. This has involved the development of equations for flame propagation, evaluation of equilibrium species concentrations and adiabatic flame temperatures together with the chemical kinetic formation

mechanism of nitric oxide. The theoretical study has been developed into a computer program which uses the experimentally measured pressure time history along with the proposed reaction mechanism to accurately predict nitric oxide formation rates.

CHAPTER II EXPERIMENTAL APPARATUS & INSTRUMENTATION

2.1 Introduction

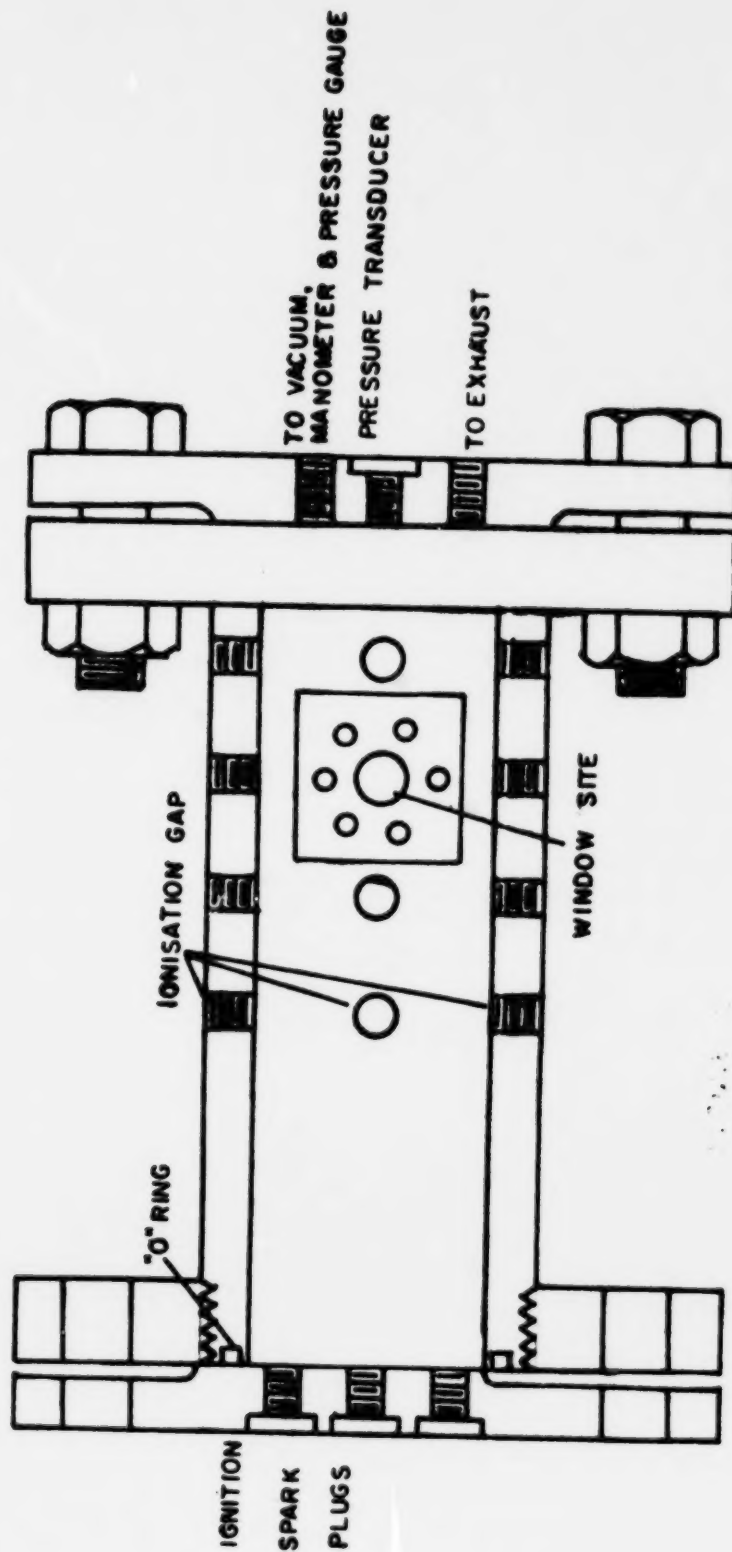
Theoretical and experimental studies referenced in article 1.1 indicate that nitric oxide formed during combustion in an internal combustion engine does not decompose to its final equilibrium composition during the subsequent expansion process. The decomposition of nitric oxide is kinetically limited and exhaust concentrations correspond to equilibrium values for temperatures approaching peak combustion temperatures rather than exhaust temperatures. The conclusion drawn is that though the decomposition of nitric oxide is kinetically slow compared to the expansion process, its formation is relatively rapid, its concentration approaching equilibrium values under certain conditions during the short combustion times available.

One purpose of the present work was to design and develop instrumentation suitable for measurement of the rapid formation of nitric oxide during combustion. With a view to exercise of better control over experimental parameters and to obtain a high degree of space and time resolution it was decided not to use the engine combustion chamber directly. A closed combustion vessel was developed instead, in which conditions similar to those occurring in an internal combustion engine could be created.

Initial estimates and subsequent measurements indicated that a time resolution of less than one millisecond would be required. Such requirements together with the questionable nature of sample composition discouraged the use of any sample extraction techniques. An evaluation of various other experimental methods indicated that the most suitable measurement technique would be time resolved ultraviolet absorption spectroscopy. The (0,0) gamma bands of nitric oxide in the vicinity of $2260 \text{ \AA}$ (13) provide a ready means of measurement of nitric oxide concentration. The apparatus and instrumentation developed for this method of measurement is now described in detail.

2.2 Combustion Vessel

The combustion vessel used in the present work consists basically of a cylinder of 4 inches internal diameter and 12 inches length. The ends of the cylinder are closed by means of flanges. Figure 2.1 illustrates the combustion vessel assembly. In the figure, the left hand end is the ignition end. In order to achieve a high degree of time resolution it was necessary to obtain a one-dimensional plane flame travelling in a direction perpendicular to the optical path. The combustion system was designed with this requirement in view. The ignition end flange is drilled and tapped to carry five spark plugs, spatially distributed to give the required flat flame front travel-



COMBUSTION BOMB ASSEMBLY

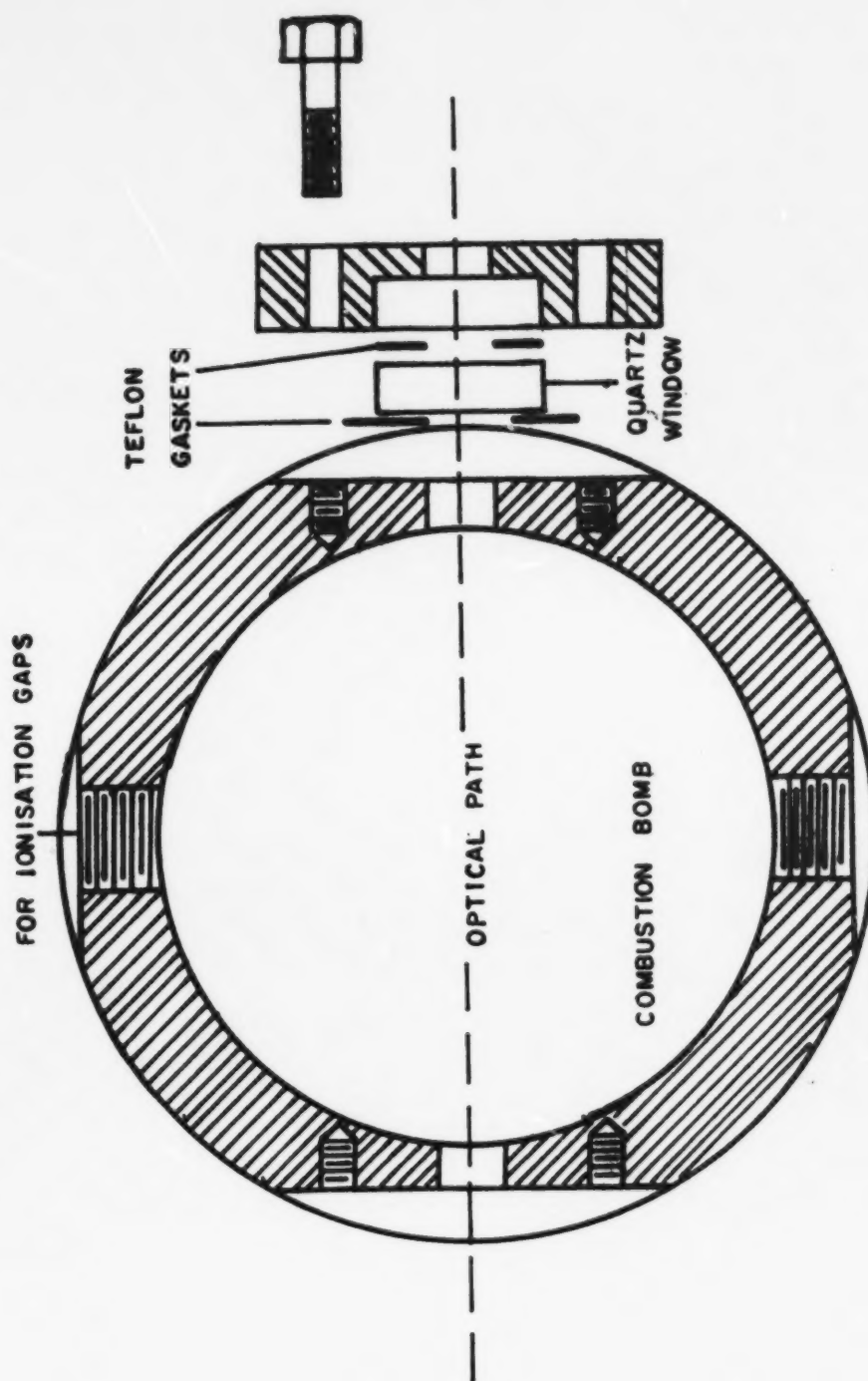
FIGURE 2-1

ling down the length of the combustion vessel from the left to the right.

Figure 2.1 also shows the window site. Figure 2.2 shows the details of the window housing and assembly on the combustion vessel. The optical path in figure 2.1 is perpendicular to the plane of the paper.

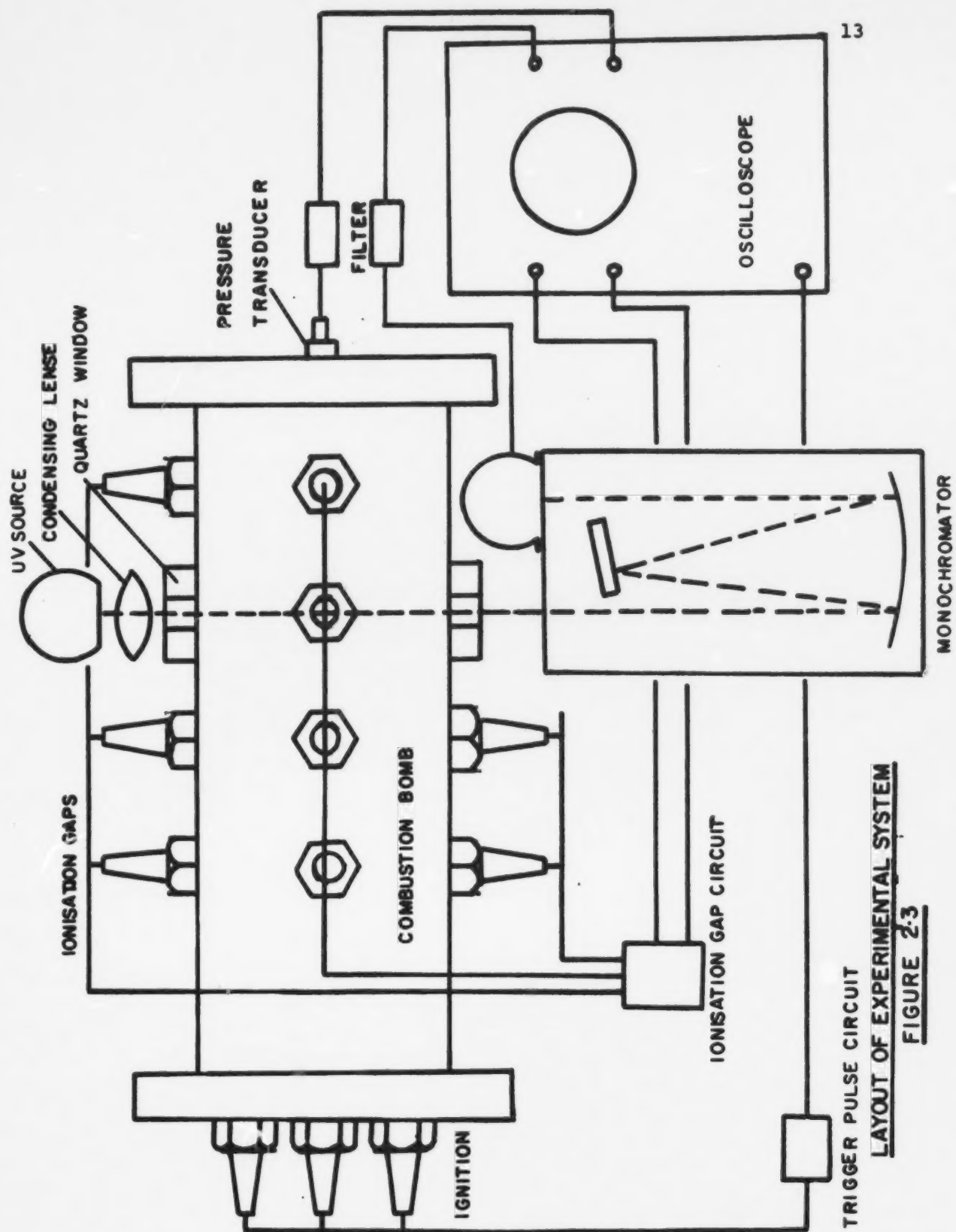
The combustion vessel is drilled and tapped at suitable locations along its length in order to carry a large number of ionization gaps. End flanges are drilled and tapped to carry suitable Swagelok tube fittings. These are used for inlet, exhaust and evacuation. One-fourth inch tubing is used to connect the combustion vessel through Swagelok fittings and valves to compressed gas bottles containing air and fuel. Similiar connections lead to a vacuum pump, pressure gauges and mercury manometer. A one inch copper pipe is used to exhaust the burnt gases. The far end flange carries a Kistler 601H pressure transducer. Pressure time records are obtained through the use of a Kistler S/N1713 charge amplifier and are displayed on an oscilloscope.

A schematic diagram of the general experimental system is shown in figure 2.3. In this figure also the left hand end of the combustion bomb is the ignition end. The flame travels the length of the tube from left to right. Progress of the flame is measured by ionization gaps and displayed on the oscilloscope. The optical path



QUARTZ WINDOW HOUSING & ASSEMBLY

FIGURE 2-2



is along a diameter of the vessel, perpendicular to the direction of flame propagation.

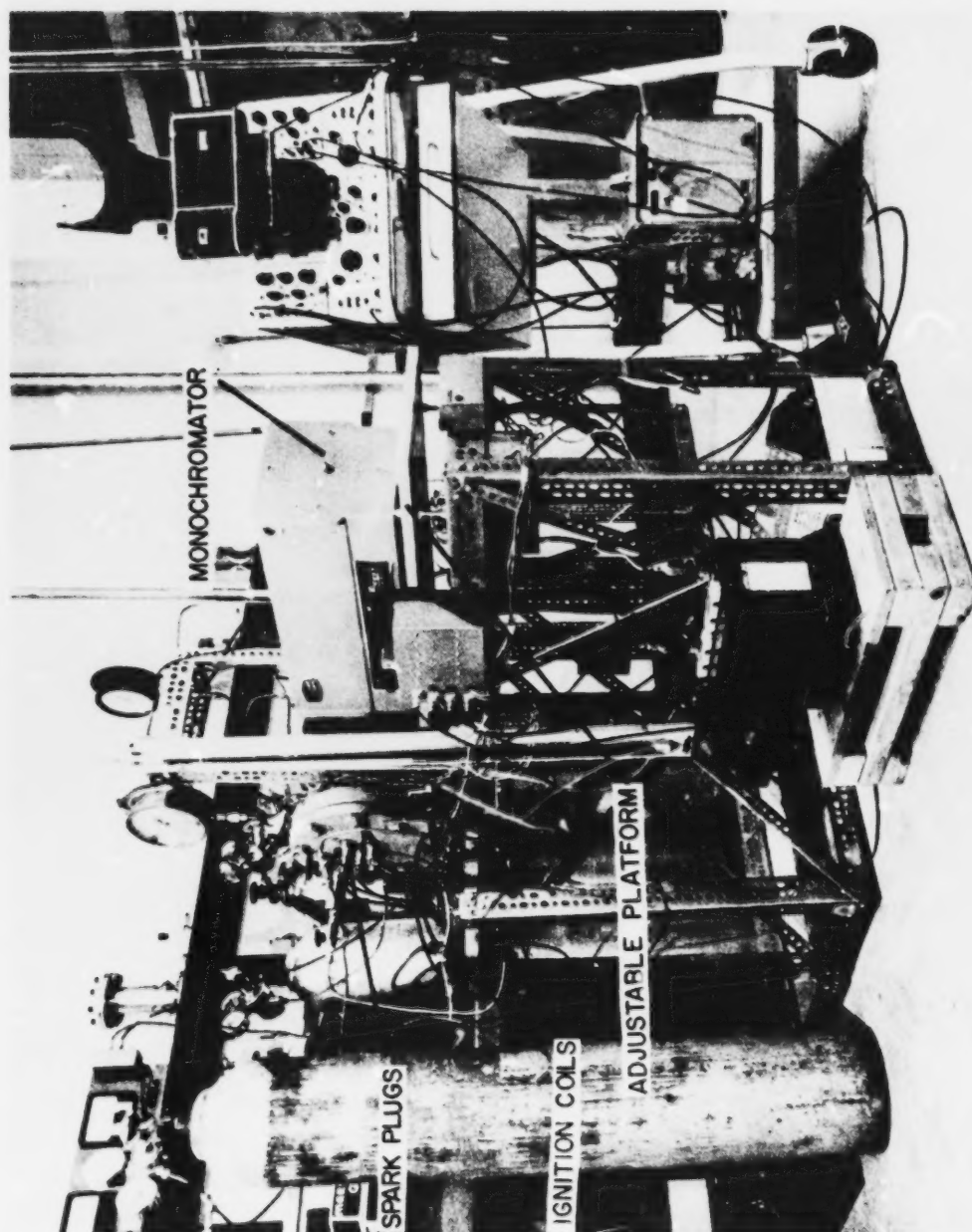
2.3 Ionization Gaps

The combustion system is equipped with a large number of ionization gaps placed both along the vessel walls and at locations within the vessel. The ion gaps are connected through appropriate circuitry (Appendix D) to several channels of a multichannel oscilloscope. The presence of the flame front at a gap is displayed as a signal peak (Figure 3.3). Ionization gap signals are used to record flame front position during experimental runs and to evaluate flame front curvature. These signals are used particularly to determine the time of flame front arrival in the optical path.

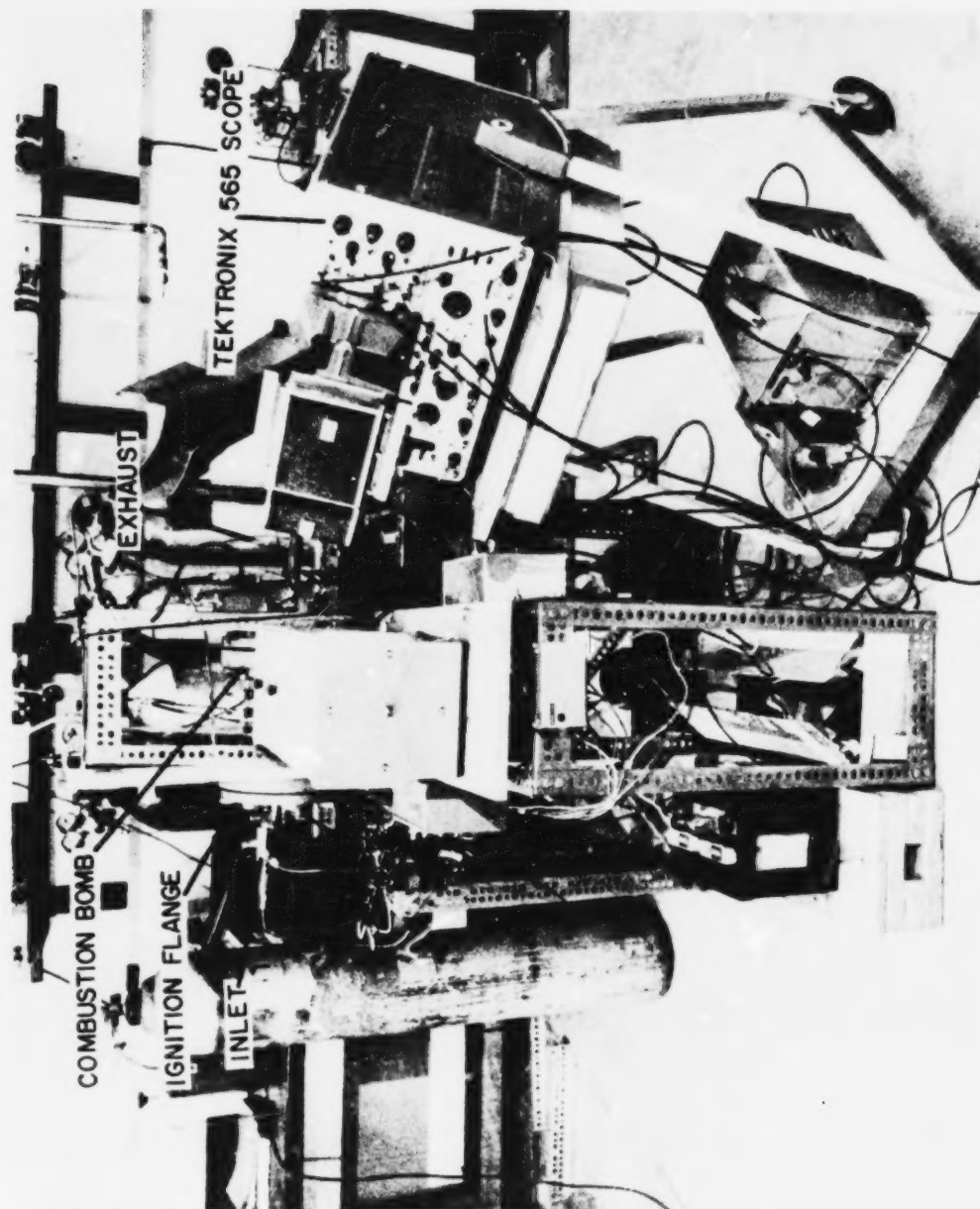
The instant of flame arrival in the optical path seen in conjunction with the absorption of ultraviolet light due to nitric oxide establishes the spatial position of nitric oxide formation reactions with respect to the flame. Further, in the present work, this event marks the zero of time from which nitric oxide formation is measured.

Standard 14 mm spark plugs are used as ion gaps. These are modified as shown in figure 2.8 to reach central locations in the combustion bomb. The details of the ionization gap circuit are described in appendix D.

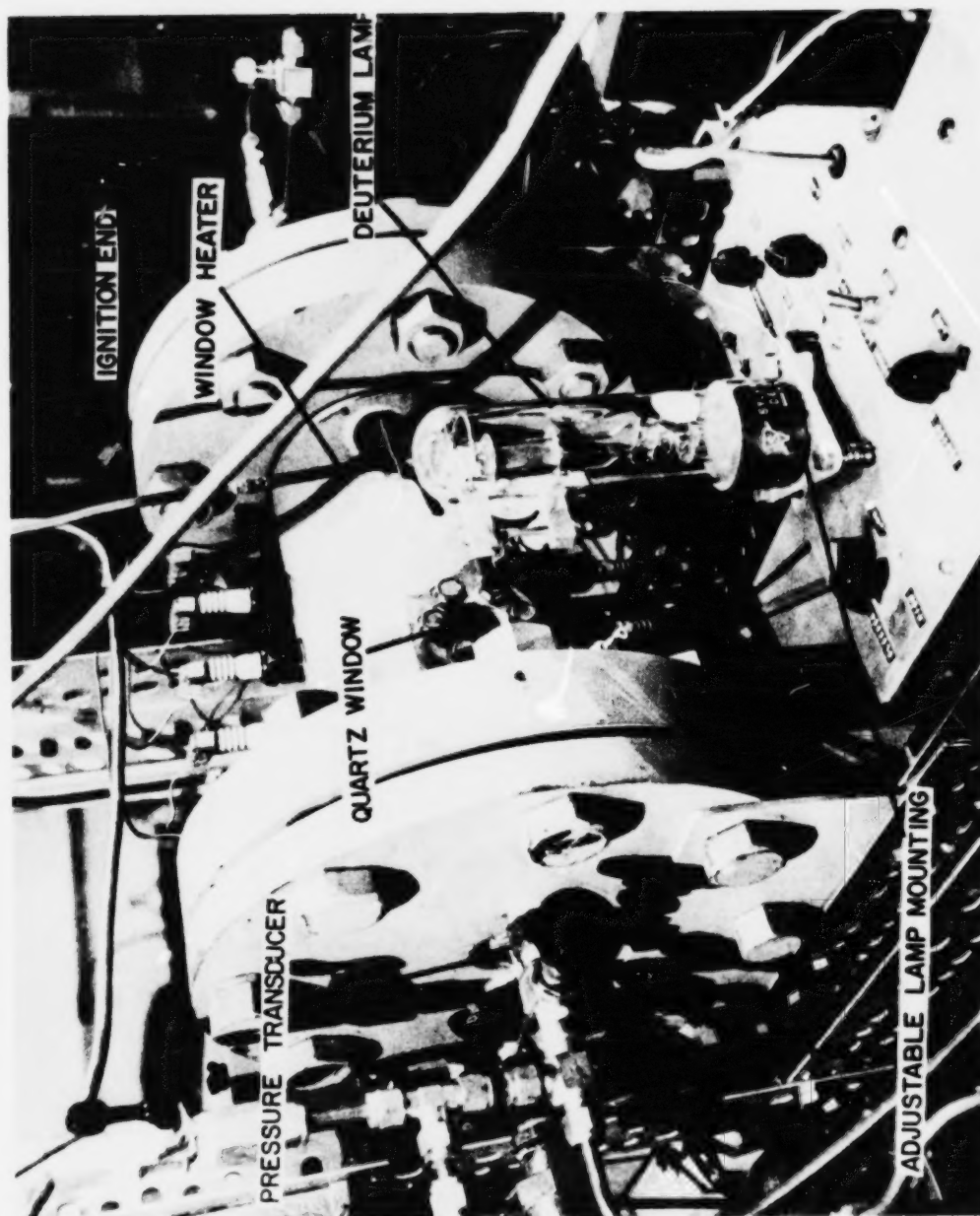
Gaps are arranged in groups located in common radial



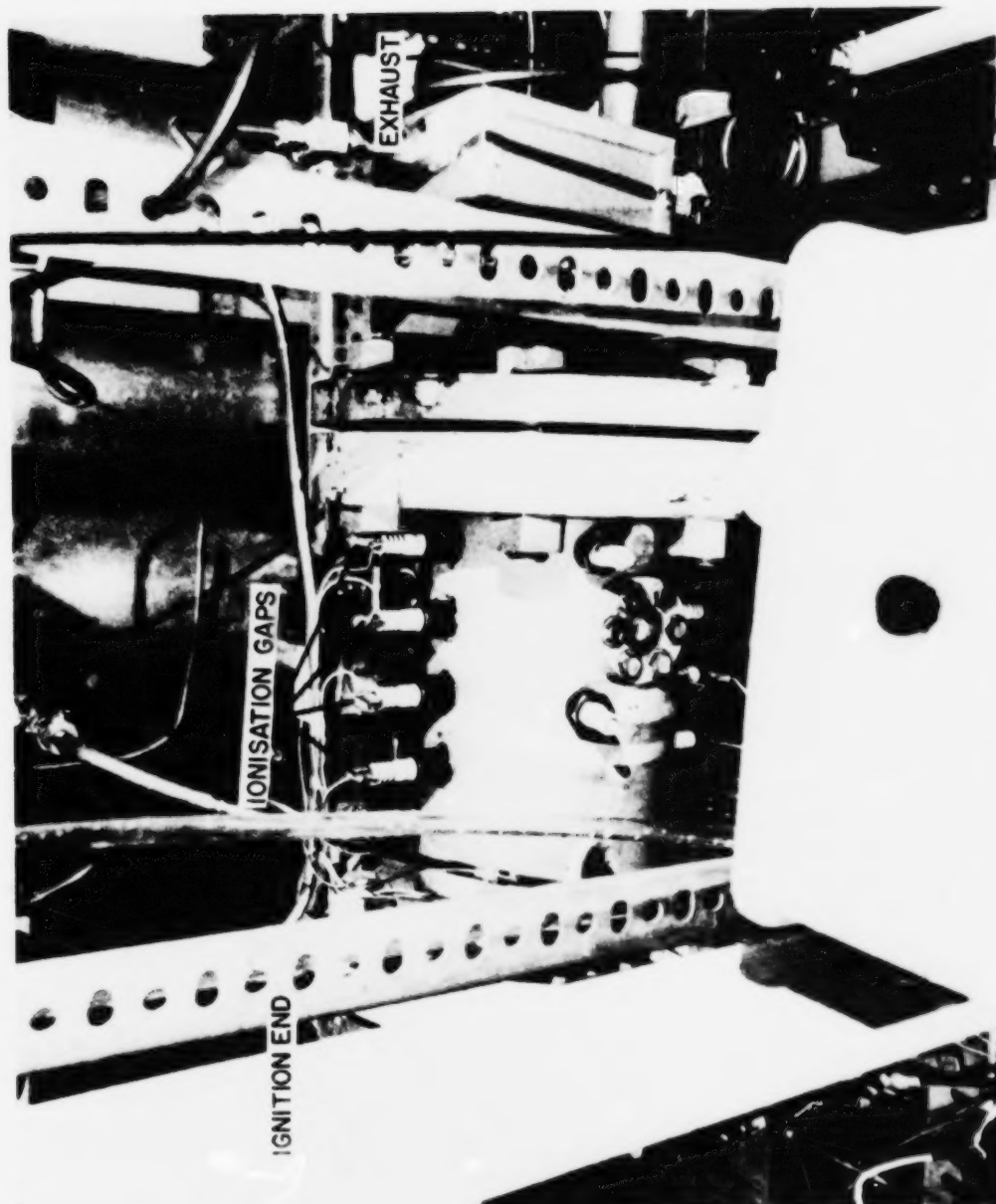
PHOTOGRAPH OF SYSTEM
FIGURE 2.4



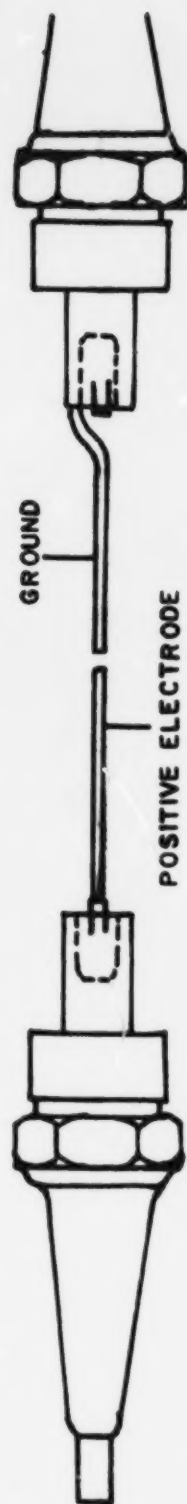
PHOTOGRAPH OF SYSTEM
FIGURE 2.5



PHOTOGRAPH OF DEUTERIUM LAMP AND MOUNTING
FIGURE 2.6



PHOTOGRAPH OF COMBUSTION BOMB
FIGURE 2.7



STANDARD 14mm SPARK PLUG

IONISATION GAPS EXTENDED TO CENTRE OF
COMBUSTION BOMB

FIGURE 2-8

planes. Thus by observing signals from one such group, flame flatness may be determined.

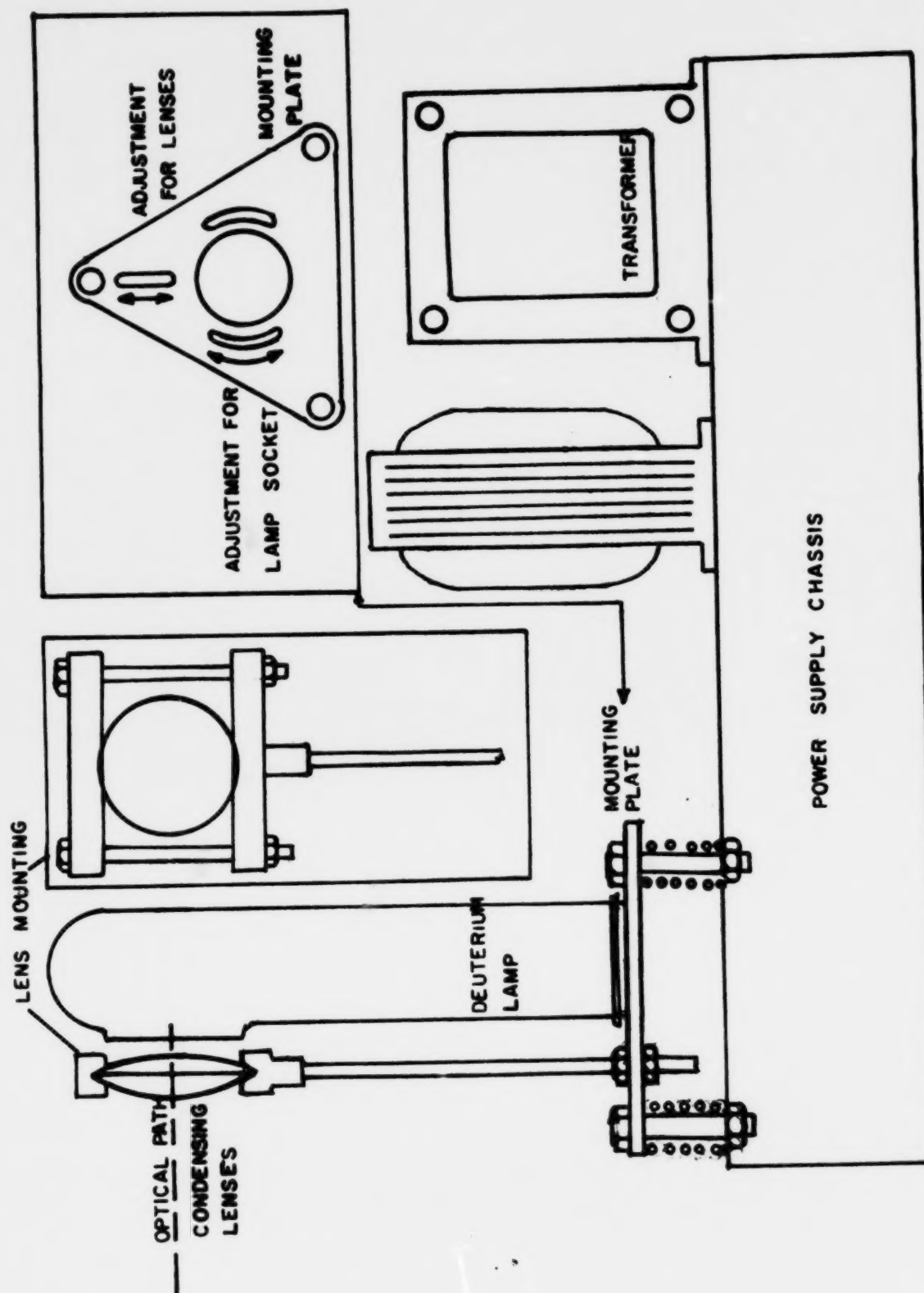
2.4 Optical System

Ultraviolet absorption spectroscopic techniques are used to measure the concentration of nitric oxide in the optical path. Figure 2.3 shows the general experimental setup. The optical path can be clearly traced in the figure. The optical path is perpendicular to the length of the tube and along a diameter.

The optical system consists of an ultraviolet light source, condensing lenses, transmission windows and monochromator.

A Sylvania DE 350 deuterium lamp is used as an ultraviolet light source. The deuterium lamp provides a continuous radiation spectrum over the wavelength range 2000 to 4000 Angstroms. The lamp requires a starting voltage of 40 Volts D.C. at 0.8 Amperes. A suitable power supply was designed and built to meet these requirements. The details of the design and circuit are given in Appendix D.

The deuterium lamp is mounted on the power supply chassis through a triangular mounting plate. The details of this mounting are shown in figure 2.9. The power supply chassis itself is mounted on an angle iron frame perpendicular to the combustion vessel as shown in figure 2.4. The inset 'A' in figure 2.9 shows the details of the mounting plate. It can be seen that the deuterium lamp

DEUTERIUM LAMP MOUNTINGFIGURE 2-9

socket can be swung about a vertical axis on the mounting plate. It can be fixed at any desired position by means of small bolts. The mounting plate position can be adjusted by means of the springs through which it is fixed to the power supply chassis. These adjustments permit the proper alignment of the optical path.

The condensing system consists of two plano-convex lenses made of ultraviolet grade quartz glass. Lenses are designed to match the F-number of the monochromator. The mounting of the lenses is shown in inset 'B' of figure 2.9. The lens frame shown in the inset is bolted to the mounting plate. Its height can be adjusted through the adjusting nuts shown. The distance of the lenses from the light source can be adjusted by moving it along the slot in the mounting plate - figure 2.9 'A'. This movement provides for adjustment in focussing.

Two diametrically opposed ultraviolet grade quartz windows are mounted on the combustion vessel. The window locations and mounting are clearly illustrated in figure 2.2. The layout of the optical system can be seen from figure 2.3. Light from the deuterium light source is focussed by the lenses through the quartz windows onto the inlet slits of a Jarrel Ash 82-000 monochromator.

The monochromator is mounted on an adjustable platform. The slit width of the monochromator can be adjusted at will.

This was maintained at a constant width of 150 μ throughout calibration and experimental runs. The monochromator uses a diffraction grating having 1180 grooves per mm. The specified dispersion is 16 Angstroms per mm. This gives a bandpass of 2.4 Angstroms for the selected slit width. The diffraction grating can be rotated until the desired frequency of light appears at the exit slit of the monochromator.

2.5 Detection System

Light from the ultraviolet light source is focussed by the condensing system and passes through the combustion vessel via two diametrically opposed quartz windows onto the inlet slits of the monochromator. The monochromator diffraction grating disperses the incident light to its component frequencies. The grating is rotated until the desired frequency of light falls on the exit slit.

Monochromatic light (more precisely of a finite bandpass-- 2.4 Angstroms in this case) emergent from the monochromator exit slits falls on a detector. The detector is a 1P 28 photomultiplier tube fixed in a leakproof case and bolted to the monochromator at the exit slit. The photomultiplier and the power supply circuit are shown in Appendix D.

The output from the photomultiplier is passed through a filter to suppress high frequency noise and fed into one channel of a multichannel oscilloscope. During operation the monochromator grating is set at the nitric oxide absorption

wavelength. A mixture of fuel and air is ignited in the combustion vessel and the flame propagates down the length. Nitric oxide formed as a result of combustion absorbs light of this wavelength. The absorption is detected by the photomultiplier and is displayed as a deflection of the oscilloscope beam.

2.6 Recording and Peripheral Instrumentation

Flame position is detected by ionization gaps and through appropriate circuitry is displayed as a series of signal peaks on the oscilloscope. The system pressure is measured by means of a Kistler 601 H pressure transducer and is also displayed on the oscilloscope. Nitric oxide concentration is measured by measuring the absorption of ultraviolet light passing through the combustion vessel. The light absorption signal is converted to an electrical signal by means of the photomultiplier and once again displayed on the oscilloscope.

The oscilloscope used in this study is a dual beam, four channel Tektronix Type 565 scope. One important feature to be considered is the zero of time measurement. In the present study the instant of flame front arrival in the optical path is chosen to be the zero of time from which all measurements are made. This instant is marked by the signal from the ionization gaps located in the plane of the optical path. It is therefore required that the oscilloscope sweep be triggered a few milliseconds before this instant.

The triggering system used works as follows. The two beams of the oscilloscope are triggered independently. Ionization gap signals which evaluate flame position and flame curvature (see article 2.3) are displayed on two channels of one beam. This beam is triggered by the ignition pulse. The ignition pulse also provides the input to a trigger pulse generator designed and built for use in this study. The pulse circuit and its design are described in Appendix D. The trigger pulse generator provides one or more (up to three) pulses with an adjustable delay interval. These pulses are used to delay the second beam of the oscilloscope, the two channels of which carry signals from the pressure transducer and the photomultiplier. The adjustable delay interval permits this beam to be triggered just before the instant of flame front arrival in the optical path. An adjustable interval is required because this instant, which is a function of flame speed is dependent on the type of fuel employed and the equivalence ratio. Further, by the use of the additional trigger pulses available a faster sweep rate may be used. A faster sweep rate would normally reduce the range of measurement. However, the trigger pulse generator provides up to three trigger pulses which can be used to trigger this beam repeatedly enabling the use of a fast sweep rate without sacrifice of range of measurement.

Oscilloscope displays are recorded by means of a polaroid camera attached to the scope.

CHAPTER III EXPERIMENTAL INVESTIGATION

3.1 Calibration

The concentration of nitric oxide in the optical path of the vessel is determined from the recorded spectral absorption due to the (0,0) gamma bands of nitric oxide near 2260 angstroms. Calibration was performed by injecting measured quantities of nitric oxide into the evacuated vessel and subsequently pressurizing it with pure nitrogen to desired levels of total pressure.

Calibration data were fit to a Beer's law type of expression having the form

$$A_{\lambda} = 1 - \exp (-K_{\lambda}cL)$$

where

A_{λ} percent spectral absorption at wavelength, λ

K_{λ} spectral absorption coefficient at wavelength,
 λ (moles/cm²)⁻¹

c concentration of nitric oxide (moles/cm³)

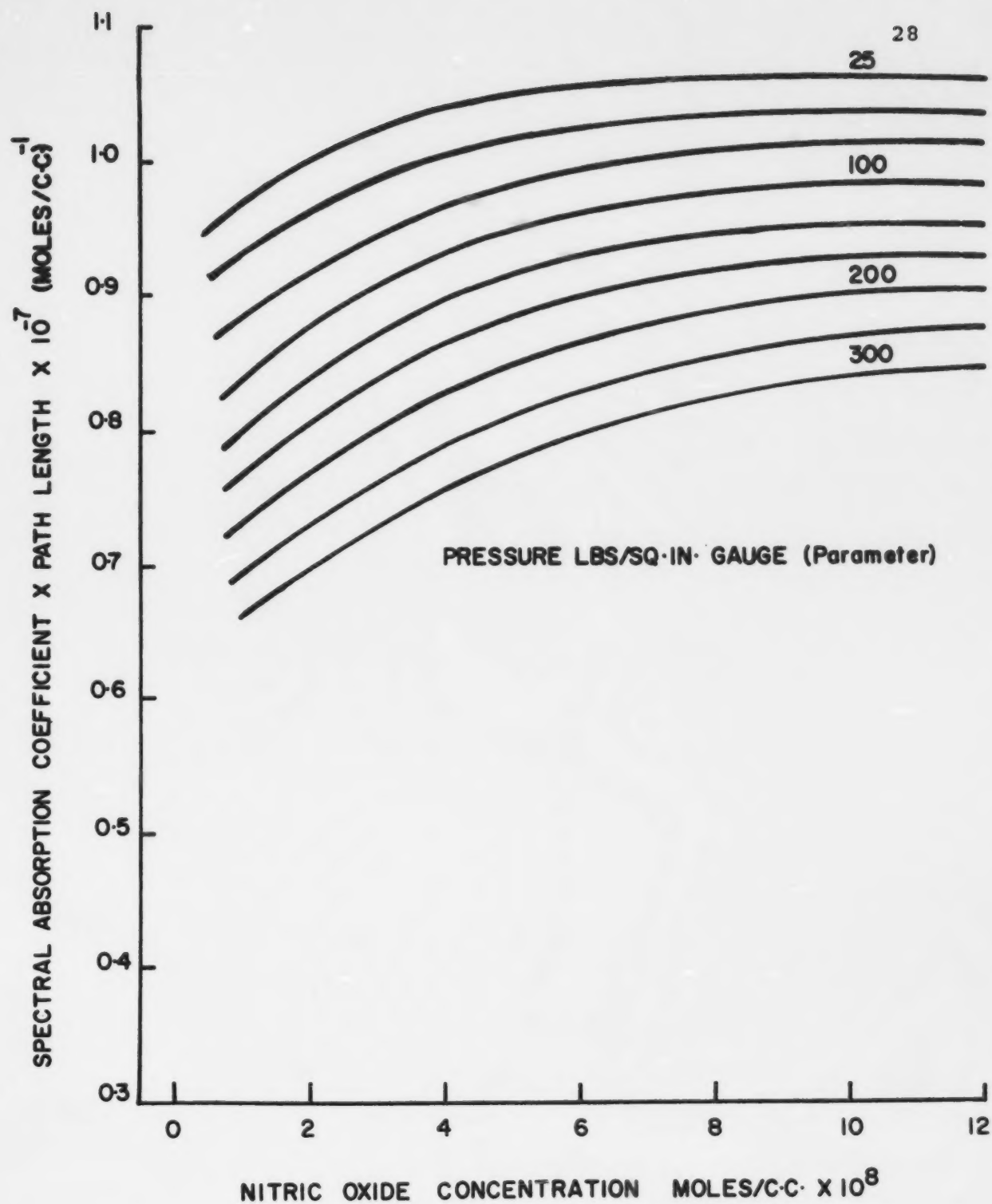
L length of optical path (cms).

The value of the spectral absorption coefficient, K_{λ} , as determined by the calibration procedure depends upon wavelength, nitric oxide concentration, total pressure and the monochromator band pass. During the calibration procedure monochromator wavelength and band pass settings were held constant at values to be used during experimental runs and the spectral absorption coefficient was plotted as a function of nitric oxide concentration and total pressure.

The values obtained from the calibration tests were used in conjunction with a suitable computer program to obtain a polynomial expression for $K_\lambda(c,p)$, the spectral absorption coefficient, with nitric oxide concentration and total pressure as independent variables. The polynomial so obtained was subsequently used for machine reduction of experimental data. The computer generated polynomial $K_\lambda(c,p)$ and the computer program used for data reduction are included in Appendix B.

Calibration was performed at room temperature. In contrast, experimental data were obtained at temperatures ranging from 2000 K to 3000 K. For this reason a temperature correction based on the equilibrium depopulation of the ground vibrational state at combustion temperatures was applied to the calibration. The calibration was further corrected for the influence of temperature on collision frequency.

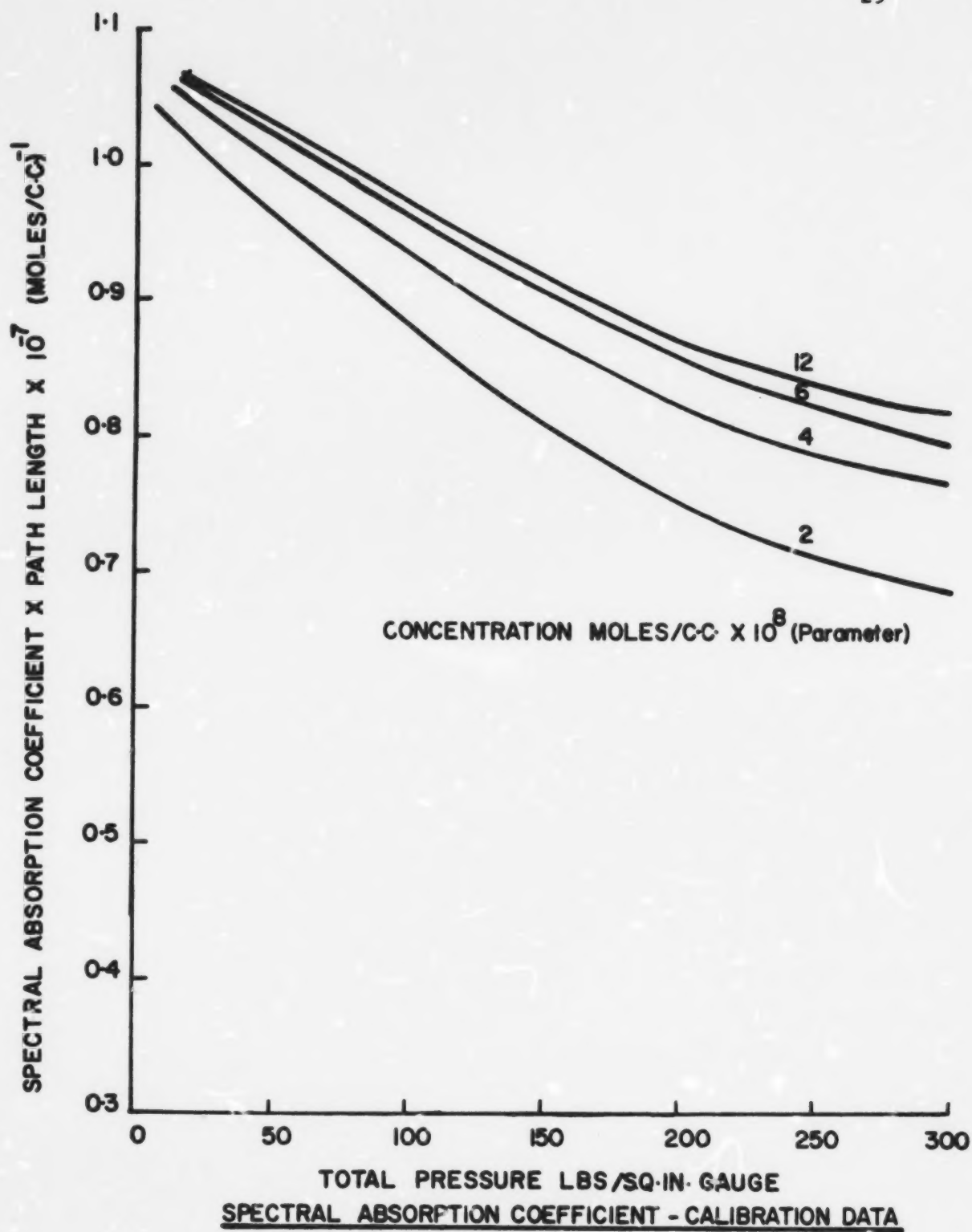
Calibration data are presented in the graphs of figures 3.1 and 3.2. In figure 3.1 the spectral absorption coefficient K_λ , is plotted as a function of nitric oxide concentration with total pressure as a parameter. The values of K_λ plotted include the length of the optical path. In figure 3.2 the same data are replotted to give the spectral absorption coefficient as a function of total pressure with concentration as a parameter. Once again the plotted values of K_λ include the length of the optical path.



NITRIC OXIDE CONCENTRATION MOLES/C.C. $\times 10^8$

SPECTRAL ABSORPTION COEFFICIENT - CALIBRATION DATA

FIGURE 3-1

FIGURE 3-2

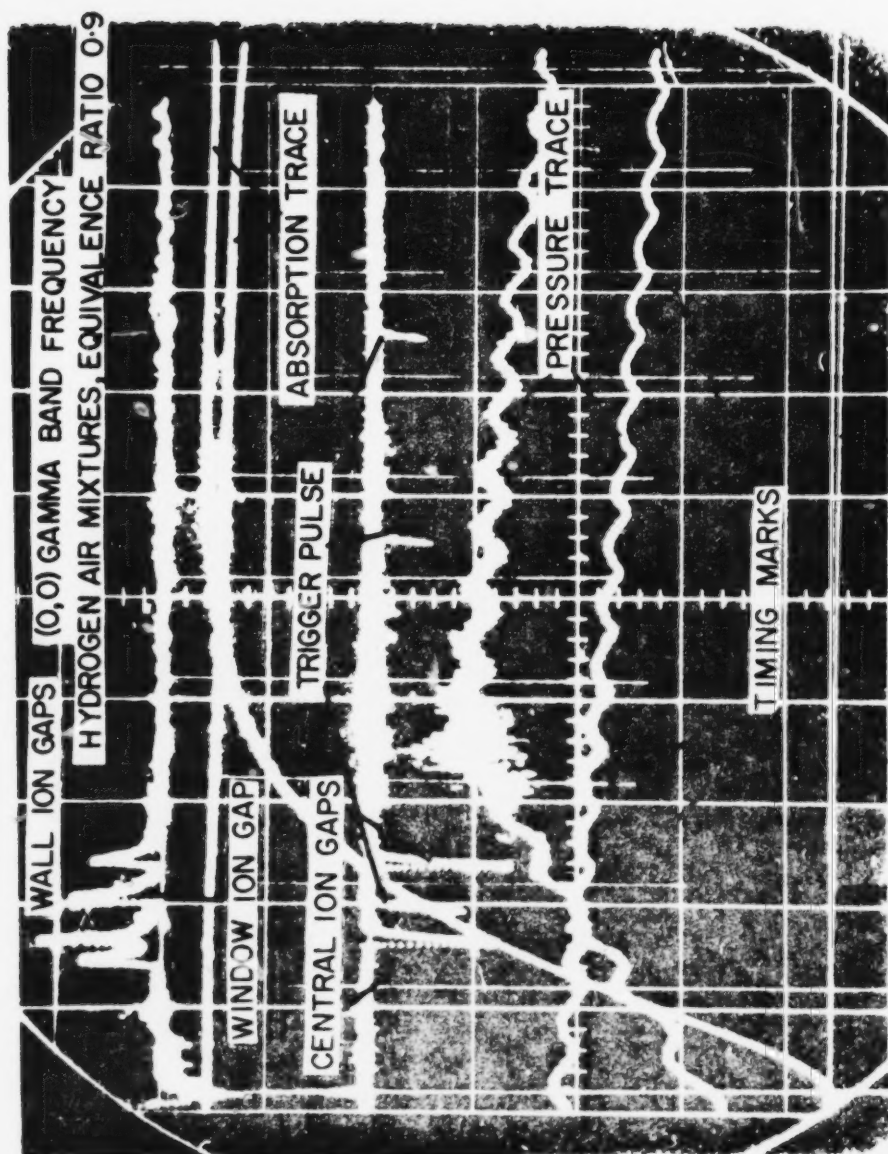
3.2 Conduct of Experiment

The combustion vessel is first evacuated and allowed to dry. It is then charged with air, fuel and diluent to their appropriate partial pressures depending upon the desired equivalence ratio and dilution. Partial pressures are monitored by means of precision pressure gauges and a mercury manometer. The gases are allowed to mix thoroughly.

The quartz windows offer a relatively cold surface on which water vapor can condense as the flame travels past the window. This can result in erroneous readings of absorption of incident light. In order to prevent this, window surfaces are kept hot by applying a narrow torch flame on the outside. Oscilloscope traces are photographed by means of a polaroid camera. A typical scope trace is shown in figure 3.3.

The mixture is ignited by means of five spark plugs spaced radially on the ignition flange so as to give a plain flame travelling axially down the combustion vessel. The oscilloscope sweep is triggered by the ignition through a pulse circuit (Appendix D).

For any given set of parameters, i.e., fuel, equivalence ratio and dilution the experiment is conducted at a number of monochromator settings in order to study the absorption at a range of wavelengths around 2260 angstroms. Data taken represents the mean of a number of successive firings at



TYPICAL OSCILLOSCOPE TRACE

FIGURE 3-3

each wavelength. At least three photographs were taken at each wavelength.

3.3 Experimental Parameters

Air-fuel ratio and temperature are two very important factors influencing the formation of nitric oxide. It was therefore decided to systematically study the following parameters;

- (1) Equivalence Ratio
- (2) Reactant Dilution
- (3) Type of Fuel

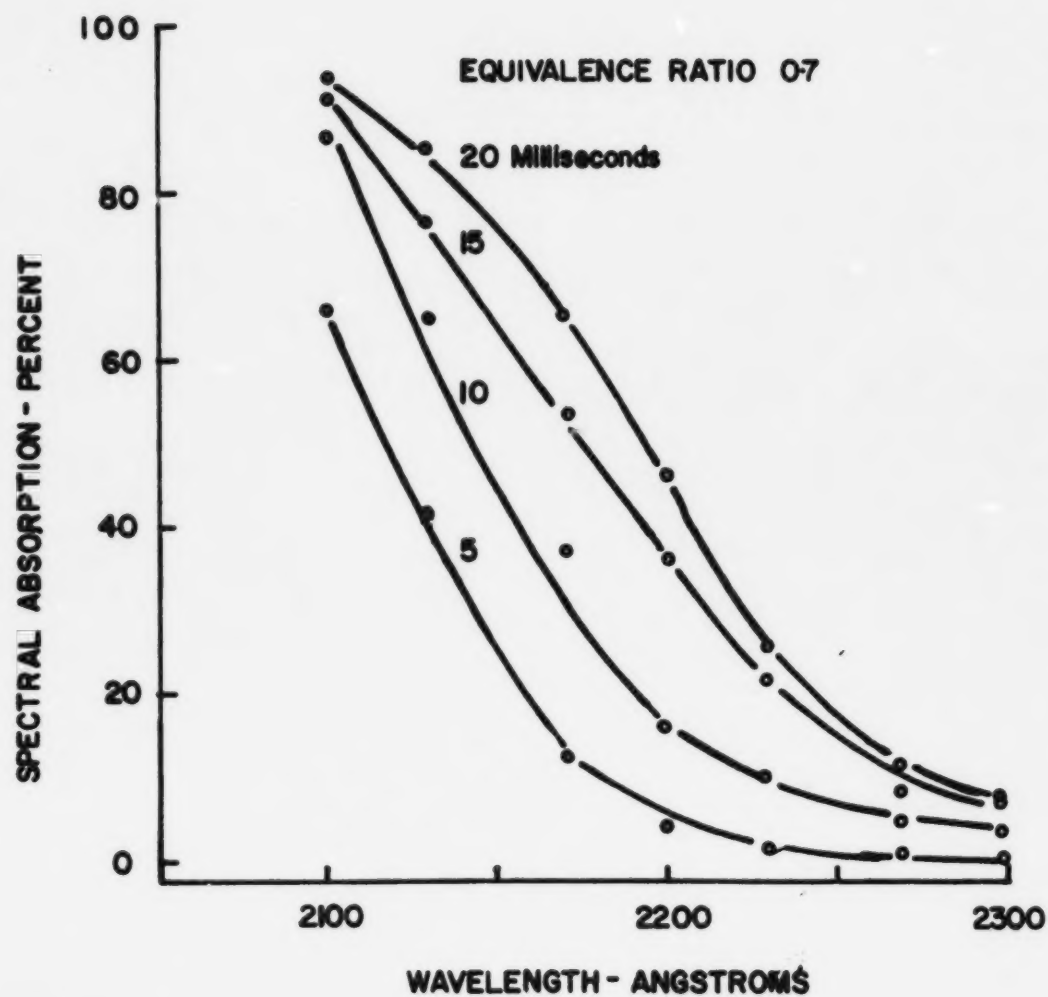
Two fuels were studied - Hydrogen and Propane. The choice of Hydrogen was dictated by the relatively complete present state of knowledge of hydrogen-air combustion kinetics. Propane was selected as a vapor phase fuel being representative of several paraffin hydrocarbons.

The effect of reactant dilution was studied in the light of some reported attempts at reducing engine exhaust concentrations of nitric oxide by means of exhaust recirculation (6,7,37). Further, such a study permits the independent evaluation of the effect of temperature on the rate of formation of nitric oxide. Nitrogen was used as a diluent.

A range of fuel-air equivalence ratios from 0.7 to 1.2 was studied for hydrogen-air mixtures.

3.4 Study of Interfering Spectra

It is well known that the Schumann-Runge bands of molecular oxygen absorb light in the vicinity of 2000 angstroms and that as the temperature of oxygen is raised this absorption extends to increasingly longer wavelength. For this reason a careful study of background absorption in the vicinity of the (0,0) gamma band of nitric oxide was performed. It was found that at the temperatures and oxygen concentrations occurring in the combustion processes studied, the Schumann-Runge system appears as a low level continuum background in the vicinity of 2260 angstroms. It has been observed by other investigators that the Schumann-Runge bands appear as a continuum under the present conditions (14). A series of typical measurements of this background absorption is plotted in figure 3.4. Here spectral absorption is plotted against wavelength for a number of elapsed times following the arrival of the flame front in the optical path. These curves were obtained from multiple firings of the system with varied monochromator wavelength settings. In the vicinity of 2260 angstroms the Schumann-Runge background absorption is low but not insignificant. For this reason all experimental runs for measurement of nitric oxide formation included simultaneous measurement of background absorption. This procedure involves multiple firings of the system with varied monochromator wavelength settings, and as a



TYPICAL BACKGROUND ABSORPTION MEASUREMENTS

FIGURE 3.4

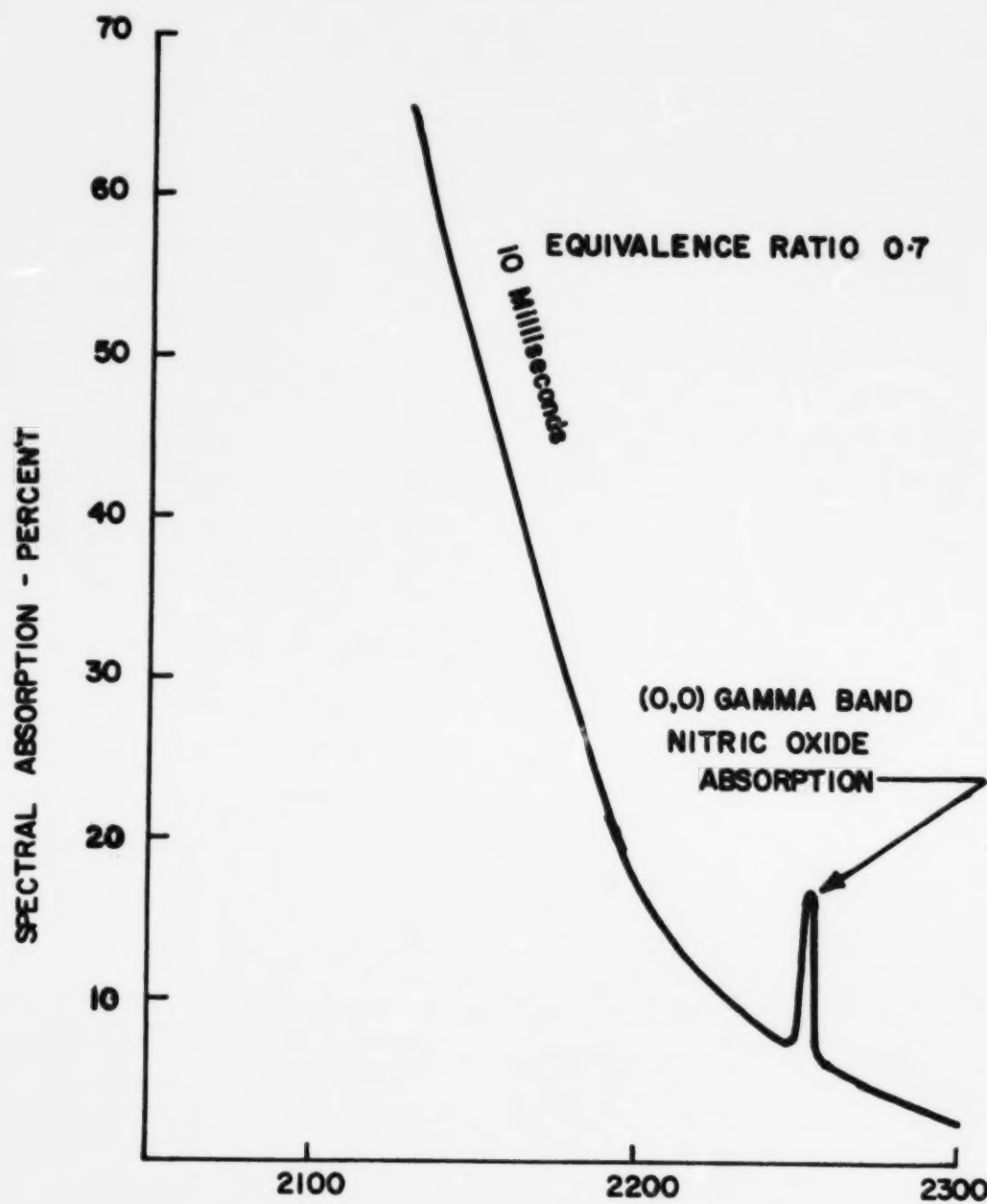
consequence, reproducibility of results from firing to firing is important. Reproducibility was studied, and it was found that spectral absorption and pressure levels for individual firings were consistent to within two percent of the average measured values for the series of repeated firings.

The relative levels of background and nitric oxide absorption are illustrated by Figure 3.5. Here measured gamma band absorption due to nitric oxide is superimposed on the measured background absorption curve. During experimental runs data similar to those plotted in Figure 3.5 were obtained for each nitric oxide determination. It was therefore possible to correct all recorded results for background absorption.

3.5 Data Reduction

The details of the data reduction procedure and the basic set of data are given in Appendix C. For any given set of parameters eg. fuel, equivalence ratio and charge dilution, the average of a large number of firings is taken. The data reduction details are discussed in Appendix C with reference to Hydrogen-air mixtures at an equivalence ratio of 0.9 at zero percent charge dilution.

Corresponding to any instant of time following the arrival of the flame front in the optical path data similar to those plotted in Figure 3.5 are taken. From



(0,0) GAMMA BAND NITRIC OXIDE ABSORPTION SUPER-
IMPOSED ON SCHUMANN-RUNGE BACKGROUND

FIGURE 3-5

these data $A_{\text{background}}$ and A_{total} at the nitric oxide gamma band frequency are determined, where $A_{\text{background}}$ represents the fractional absorption due to hot oxygen alone while A_{total} represents the total fractional absorption due to nitric oxide and hot oxygen. Background correction is effected by a logarithmic subtraction based on the following equations.

$$A_{\text{background}} = 1 - \exp(-K_{\text{background}} C_{\text{oxygen}} L) \quad 3.5-1$$

$$A_{\text{total}} = 1 - \exp(-K_{\text{background}} C_{\text{oxygen}} L - K_{\lambda} C_{\text{NO}} L) \quad 3.5-2$$

Rearrangement and subtraction of equation 3.5-1 from 3.5-2 gives

$$C = \frac{1}{K_{\lambda}(C,p)} \ln \left(\frac{1 - A_{\text{background}}}{1 - A_{\text{total}}} \right) \quad 3.5-3$$

Equation 3.5-3 is then solved for C by means of an iterative Newton-Raphson procedure employing the polynomial function $K_{\lambda}(c,p)$ generated during system calibration.

3.6 Experimental Results

The basic data obtained from photographs of oscilloscope traces and a sample data reduction are included in Appendix C. Experimental results presented here are obtained using these data and the method of data reduction indicated.

Figures 3.6 through 3.10 show pressure traces obtained through the use of the pressure transducer. The

pressure traces shown in these figures are for hydrogen-air mixtures for fuel-air equivalence ratios ranging from 0.7 to 1.2. Figures 3.11 through 3.15 show nitric oxide concentrations for the same conditions as above. Each data point represents the result of calculations outlined in Appendix C. In both sets of figures the zero of time represents the instant of flame front arrival in the optical path.

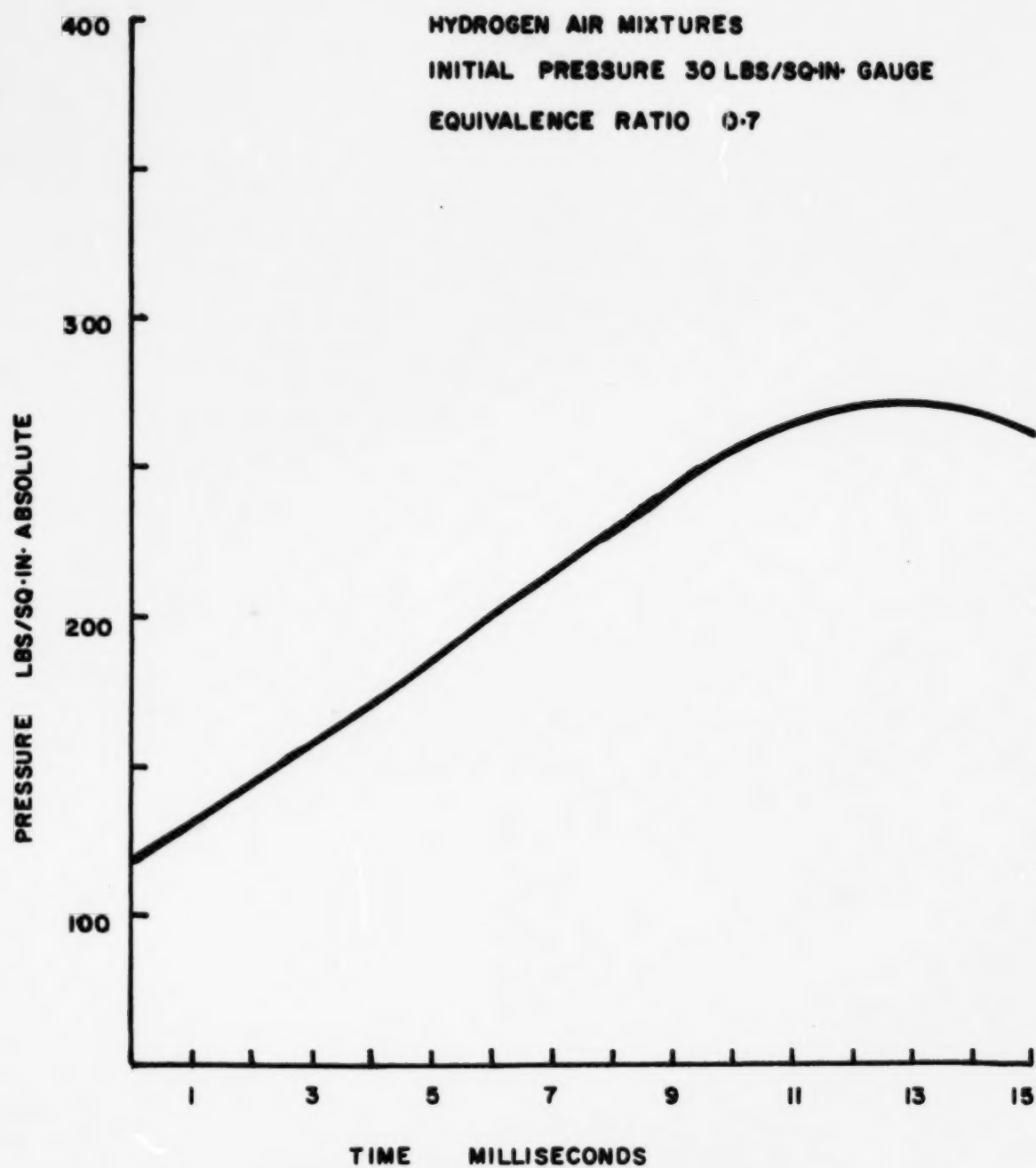
It is readily seen from the experimental results that the formation of nitric oxide is a post flame phenomenon since all measurable nitric oxide is found after the, chosen zero of time, that is, after the arrival of the flame front in the optical path. Further, the rate of formation of nitric oxide is a maximum in the vicinity of fuel-air equivalence ratio 0.9.

Figures 3.16 and 3.17 show pressure traces for propane air mixtures at equivalence ratios of 0.8 and 0.9. Nitric oxide concentration-time data for these conditions are shown in figures 3.18 and 3.19.

The effect of charge dilution is shown in figures 3.20 through 3.23. Figures 3.20 and 3.21 show pressure traces for hydrogen-air-diluent mixtures at fuel-air equivalence ratios of 0.8 and 0.9 at ten percent charge dilution. Figures 3.22 and 3.23 show nitric oxide concentration-time data for these conditions.

The results of experimental measurement of nitric

oxide concentration in propane-air and hydrogen-air diluent mixtures further confirm the conclusion that nitric oxide formation is a post flame phenomenon. The broader conclusion that can be drawn from these results are discussed in Chapter V.



EXPERIMENTAL PRESSURE-TIME HISTORY

FIGURE 3-6

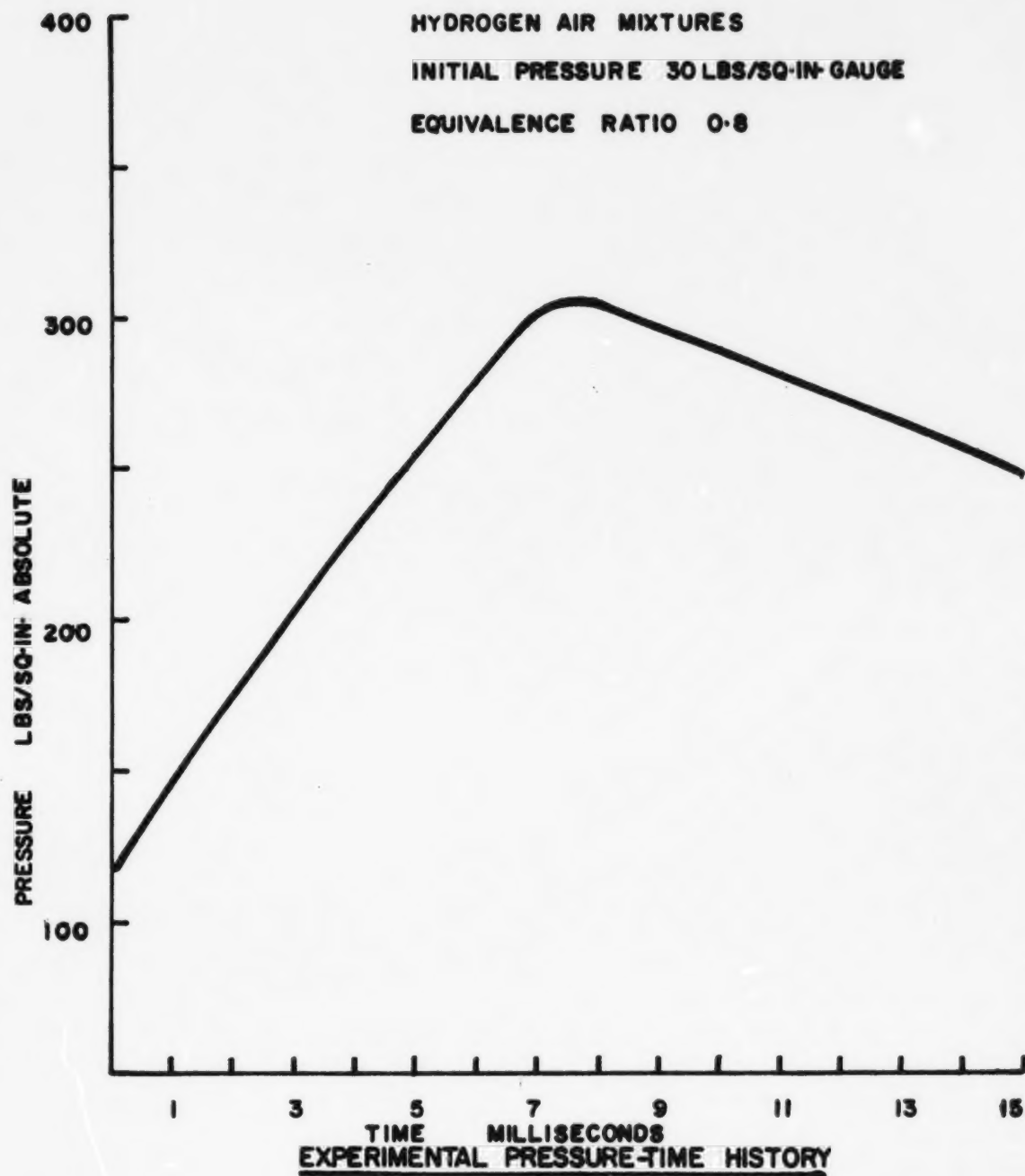
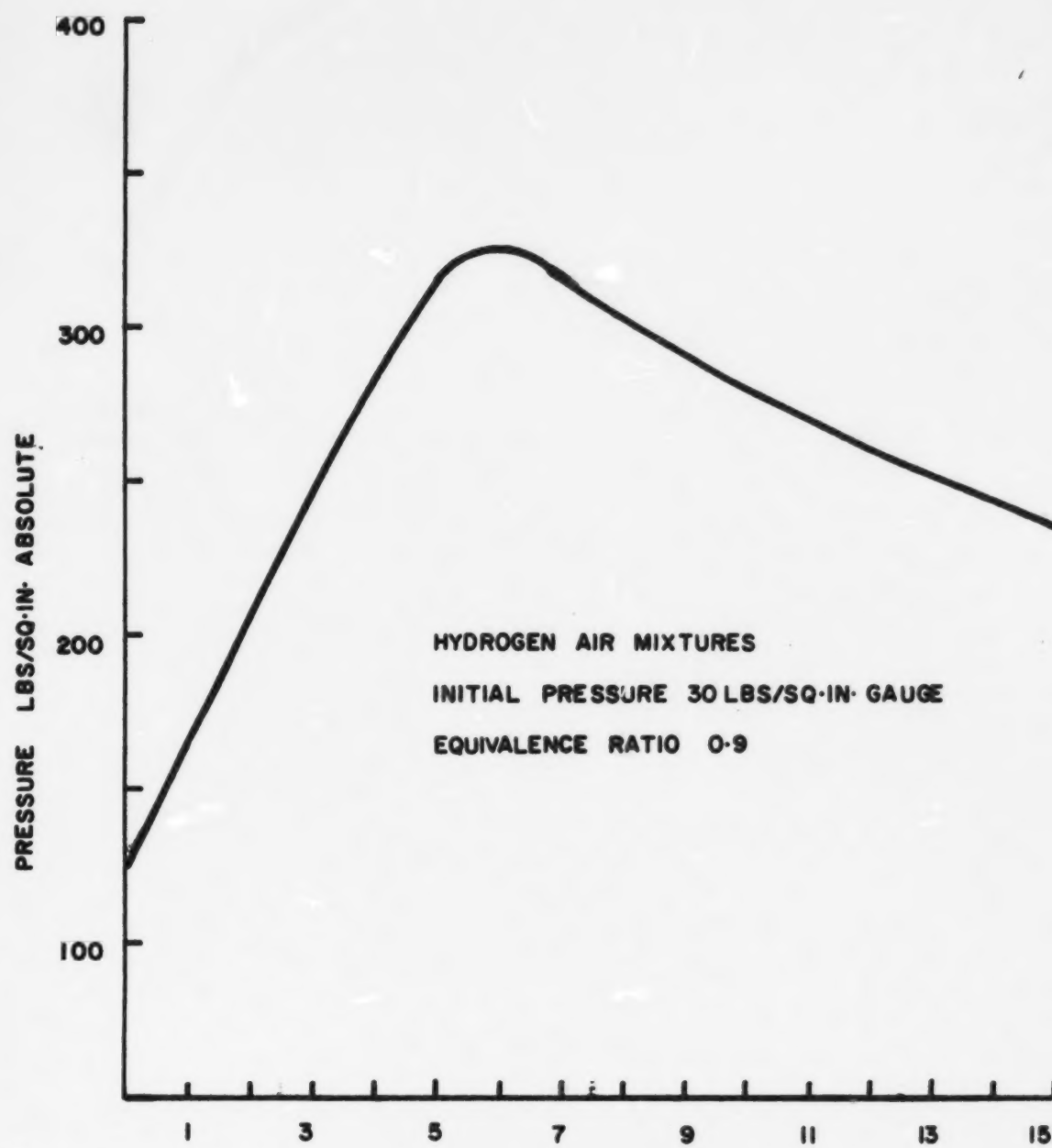
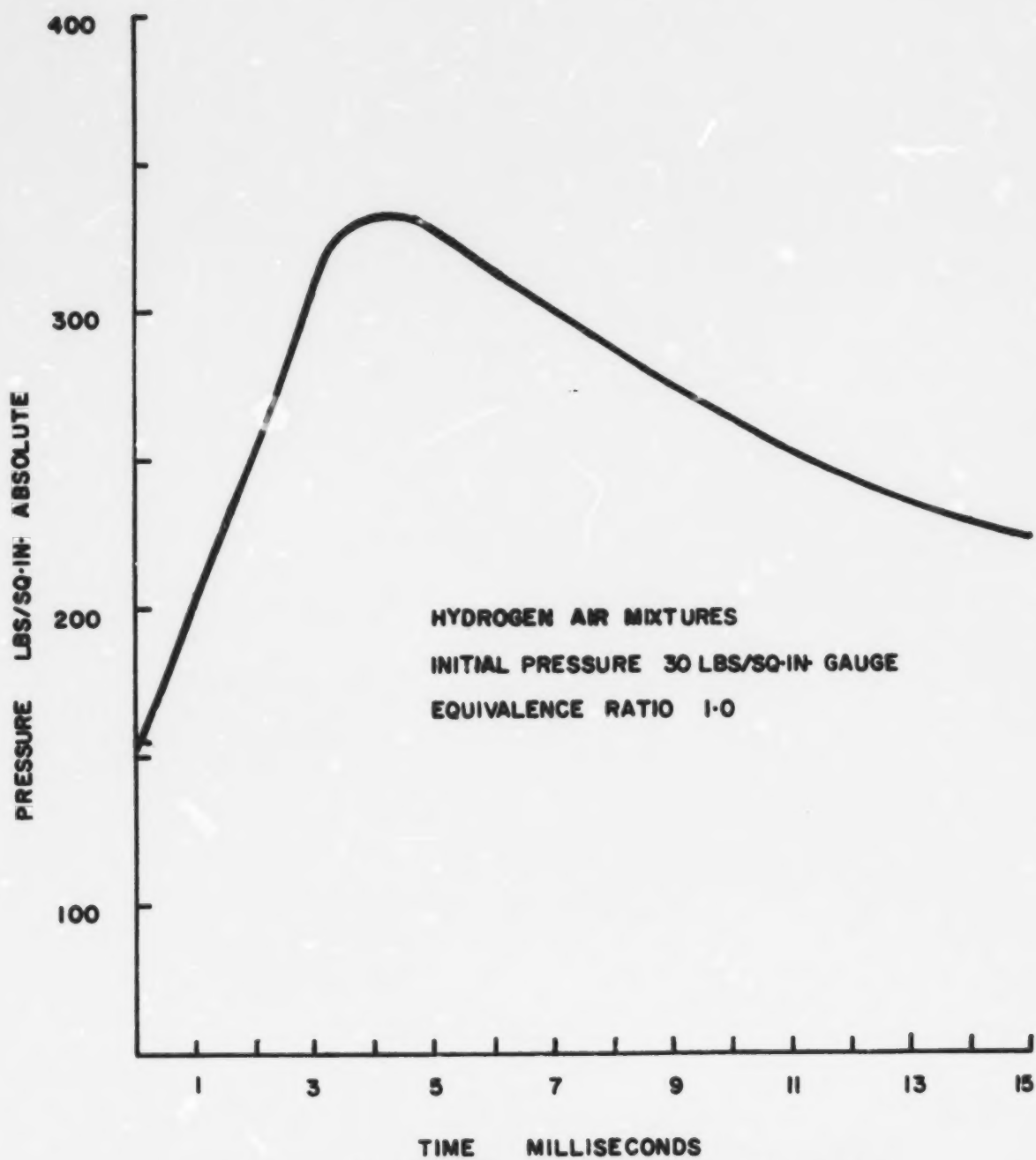


FIGURE 3-7

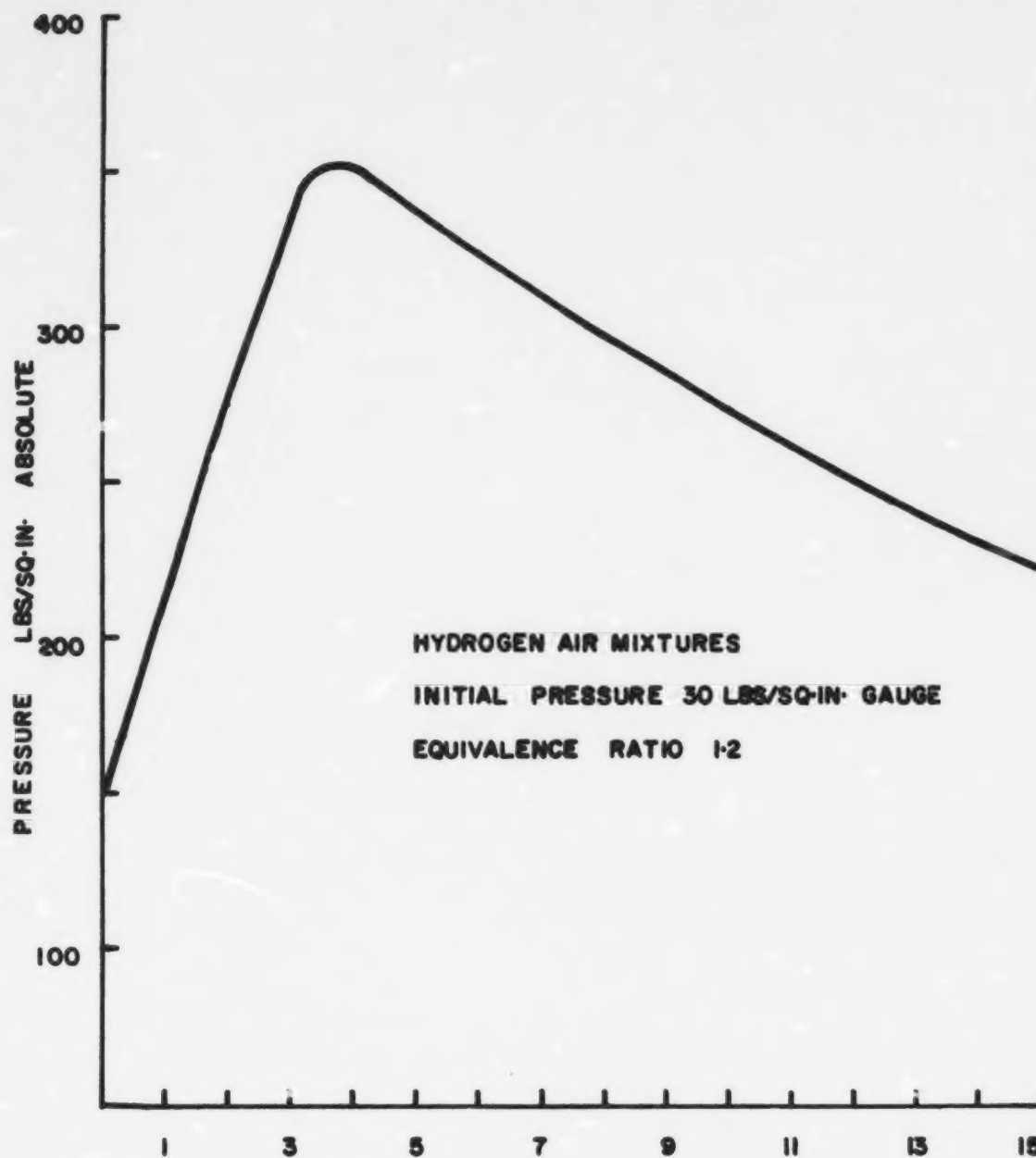


TIME MILLISECONDS
EXPERIMENTAL PRESSURE-TIME HISTORY
FIGURE 3-8



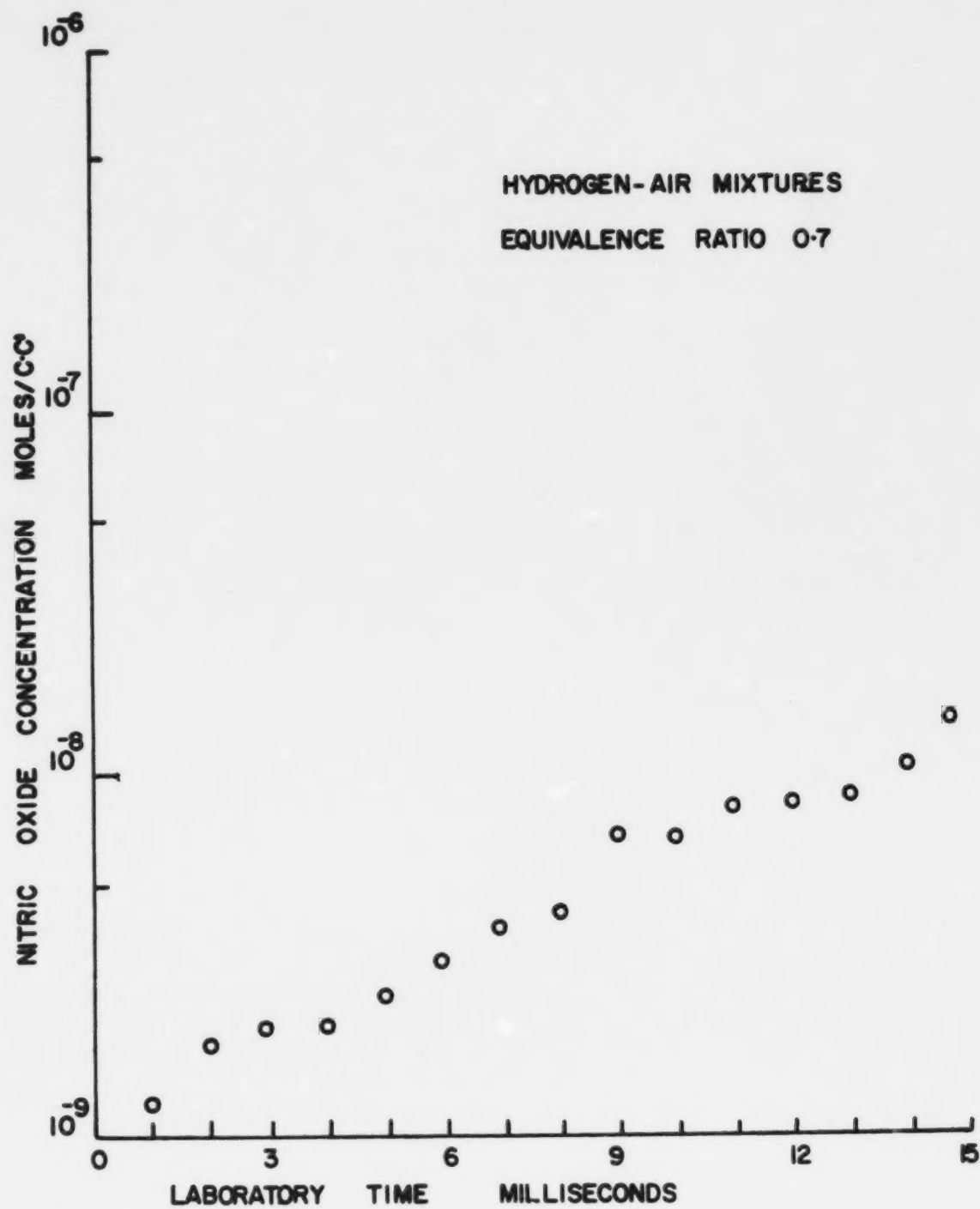
TIME MILLISECONDS
EXPERIMENTAL PRESSURE-TIME HISTORY

FIGURE 3-9



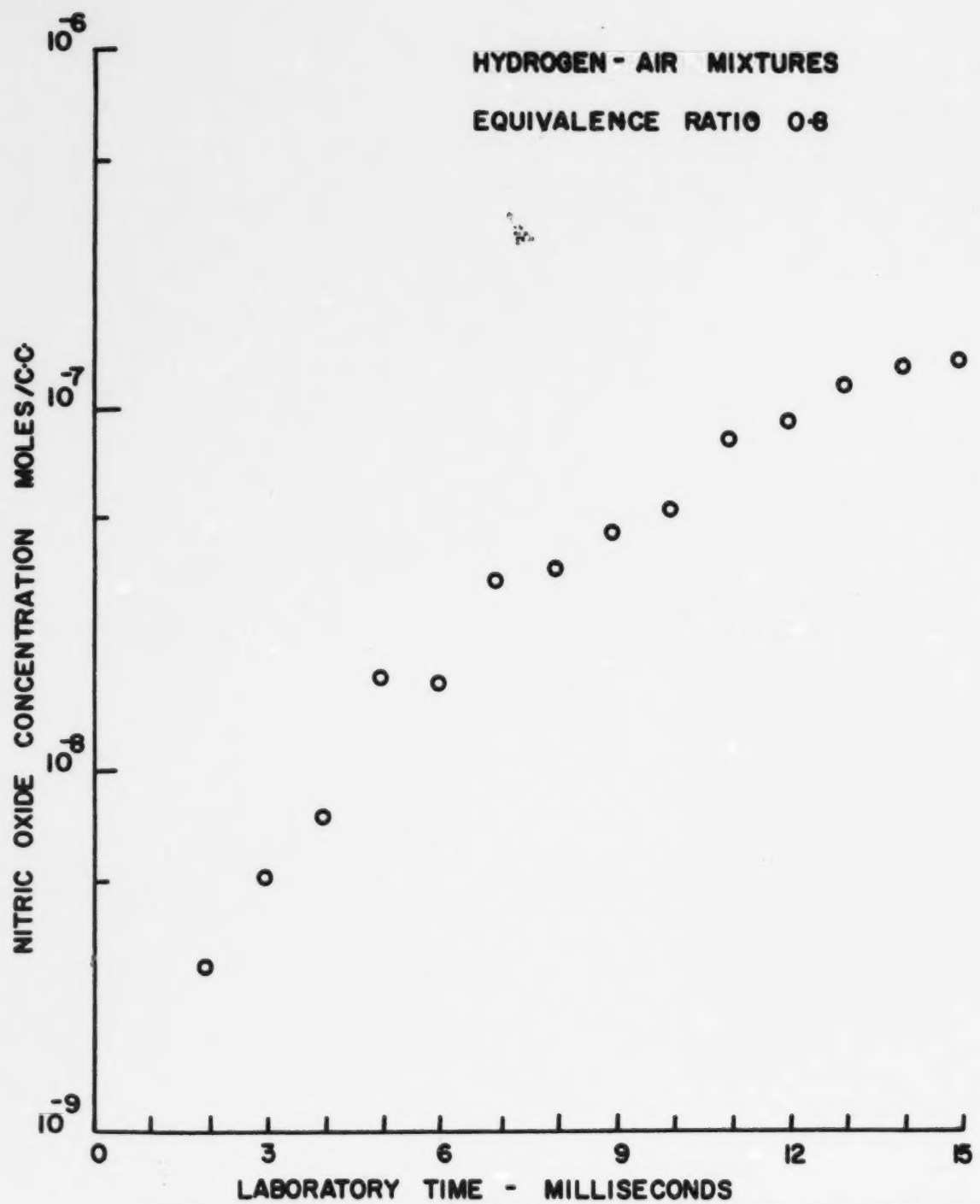
TIME MILLISECONDS
EXPERIMENTAL PRESSURE-TIME HISTORY

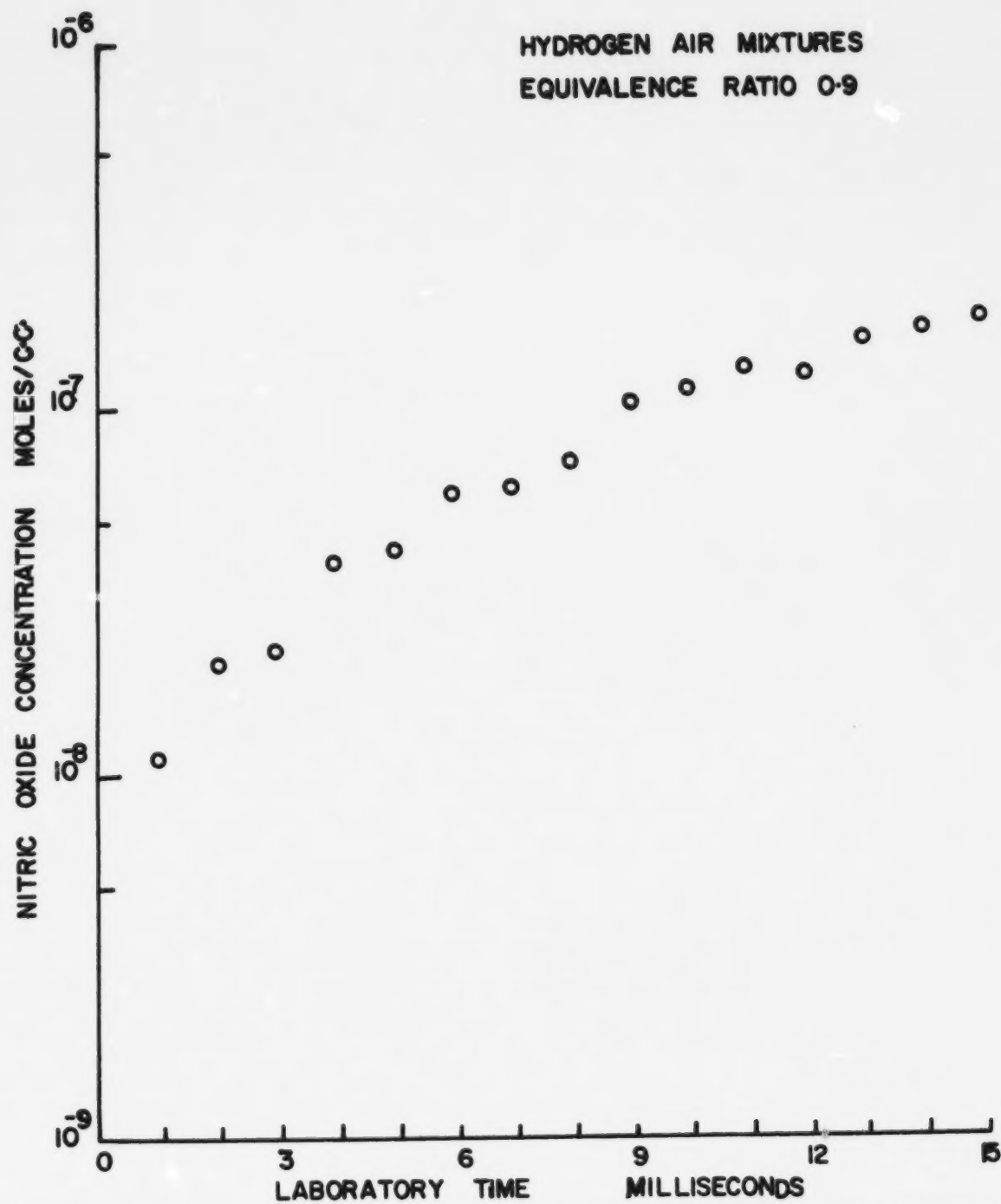
FIGURE 3-10



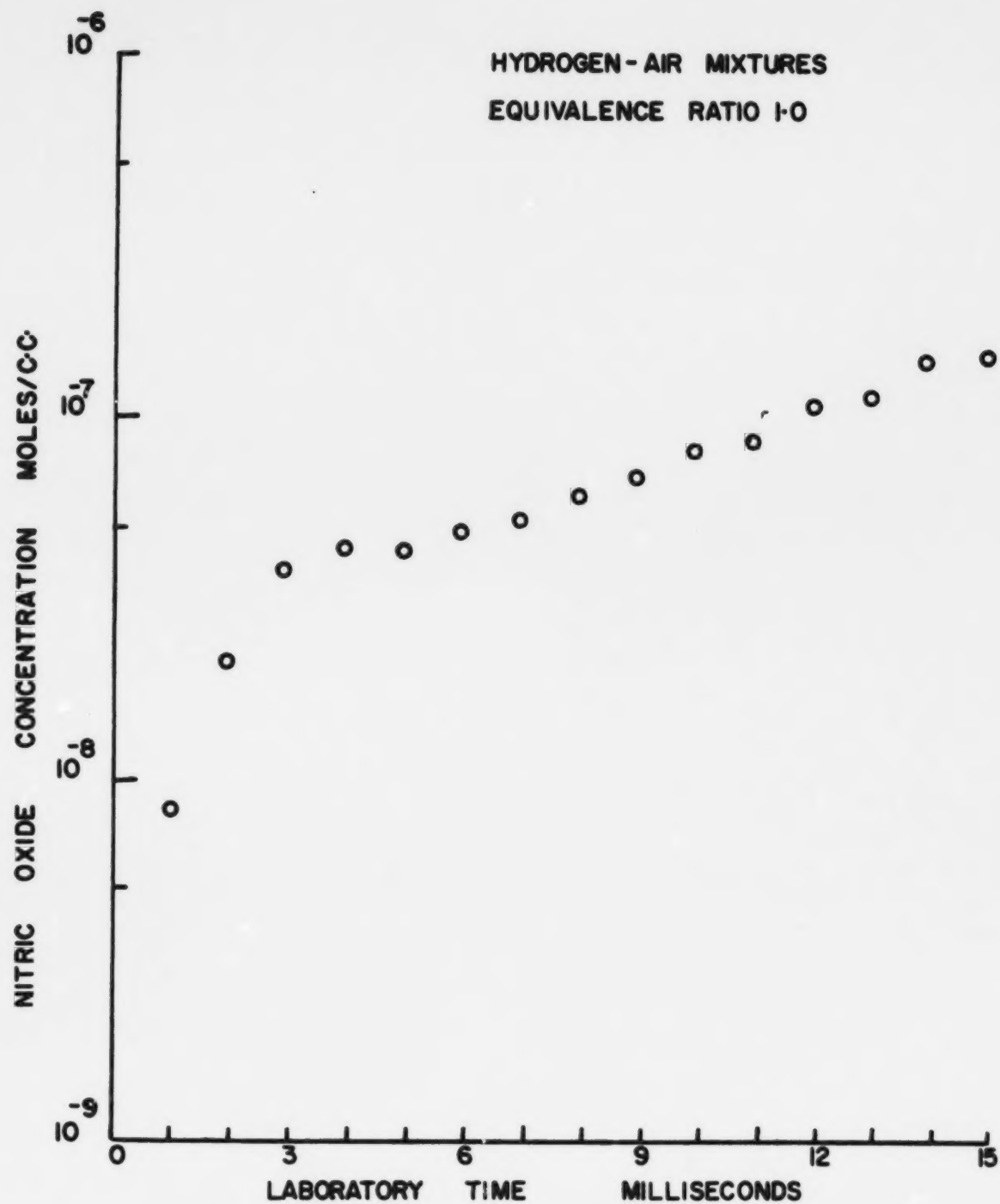
NITRIC OXIDE: EXPERIMENTAL CONCENTRATION - TIME HISTORY

FIGURE 3-11

FIGURE 3-12

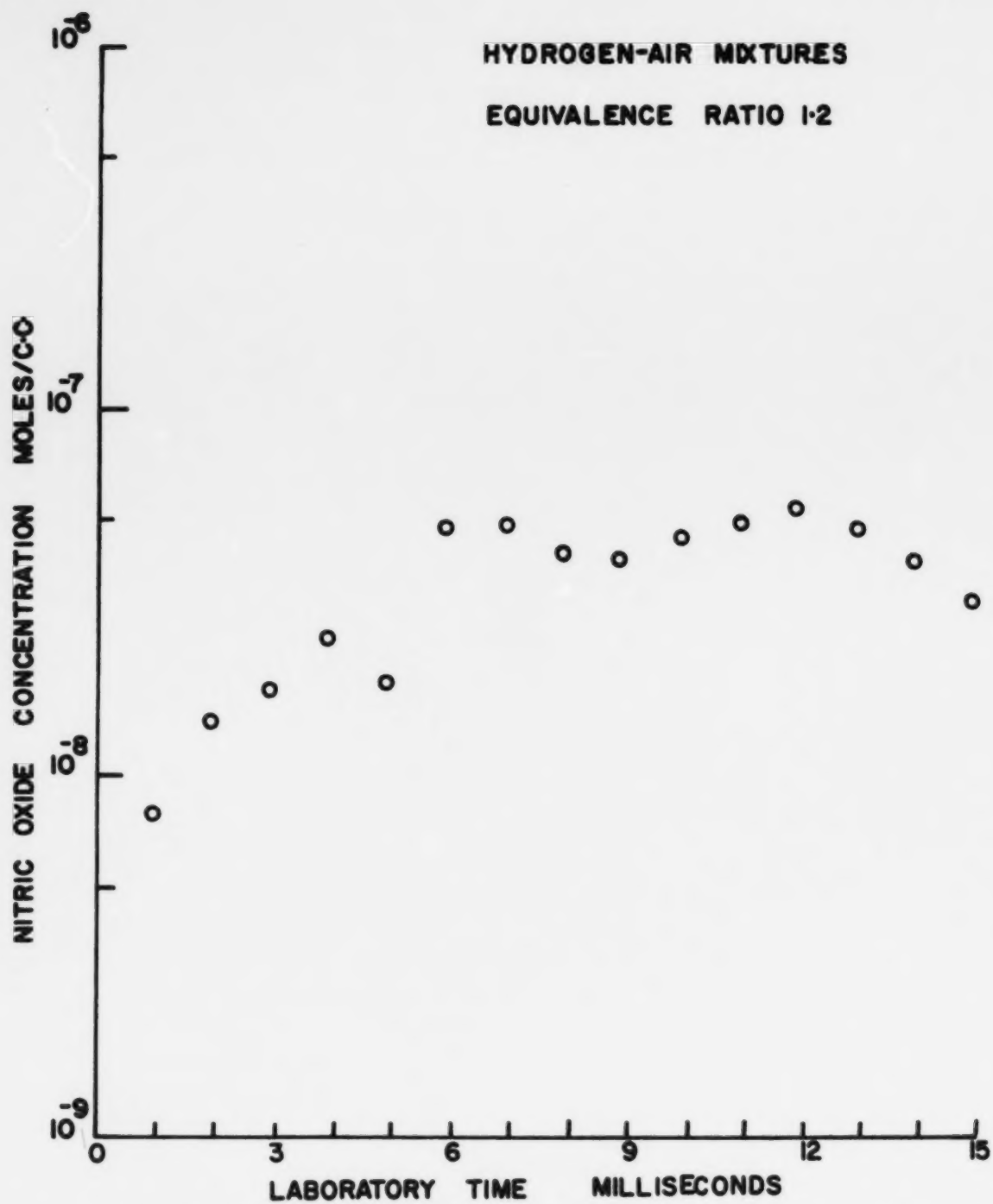


NITRIC OXIDE : EXPERIMENTAL CONCENTRATION-TIME HISTORY
FIGURE 3.13



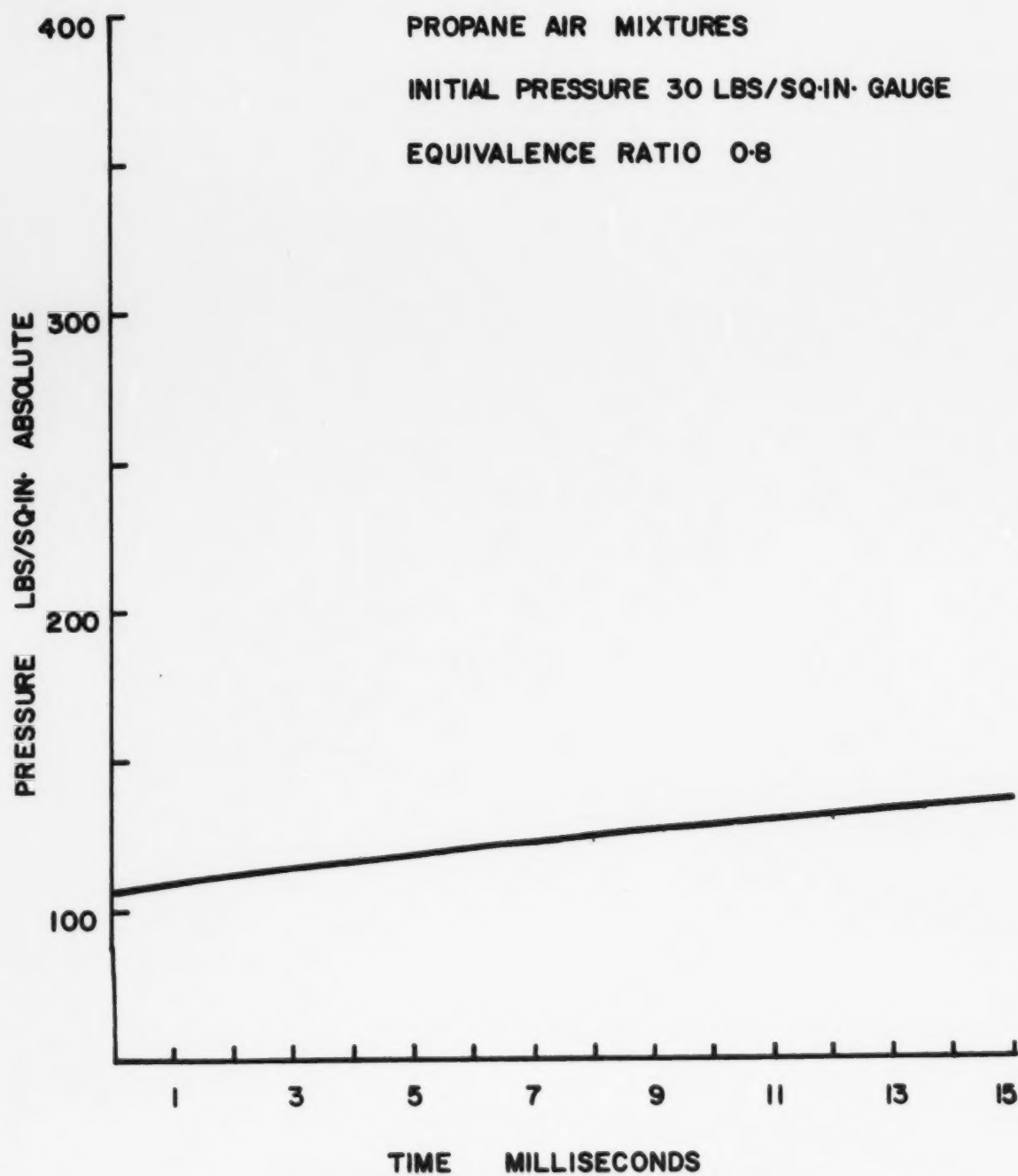
NITRIC OXIDE : EXPERIMENTAL CONCENTRATION-TIME HISTORY

FIGURE 3-14



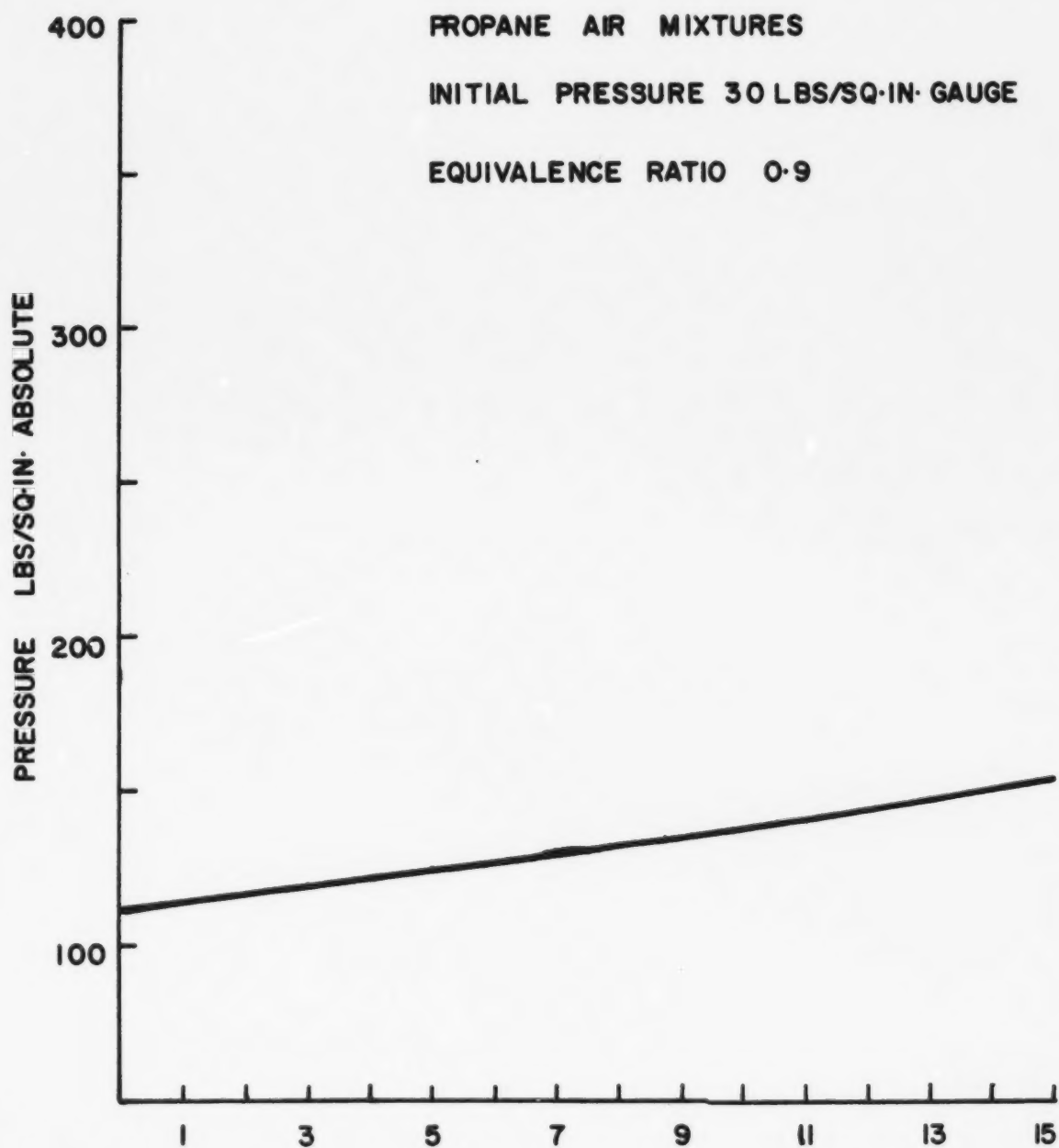
NITRIC OXIDE : EXPERIMENTAL CONCENTRATION-TIME HISTORY

FIGURE 3-15



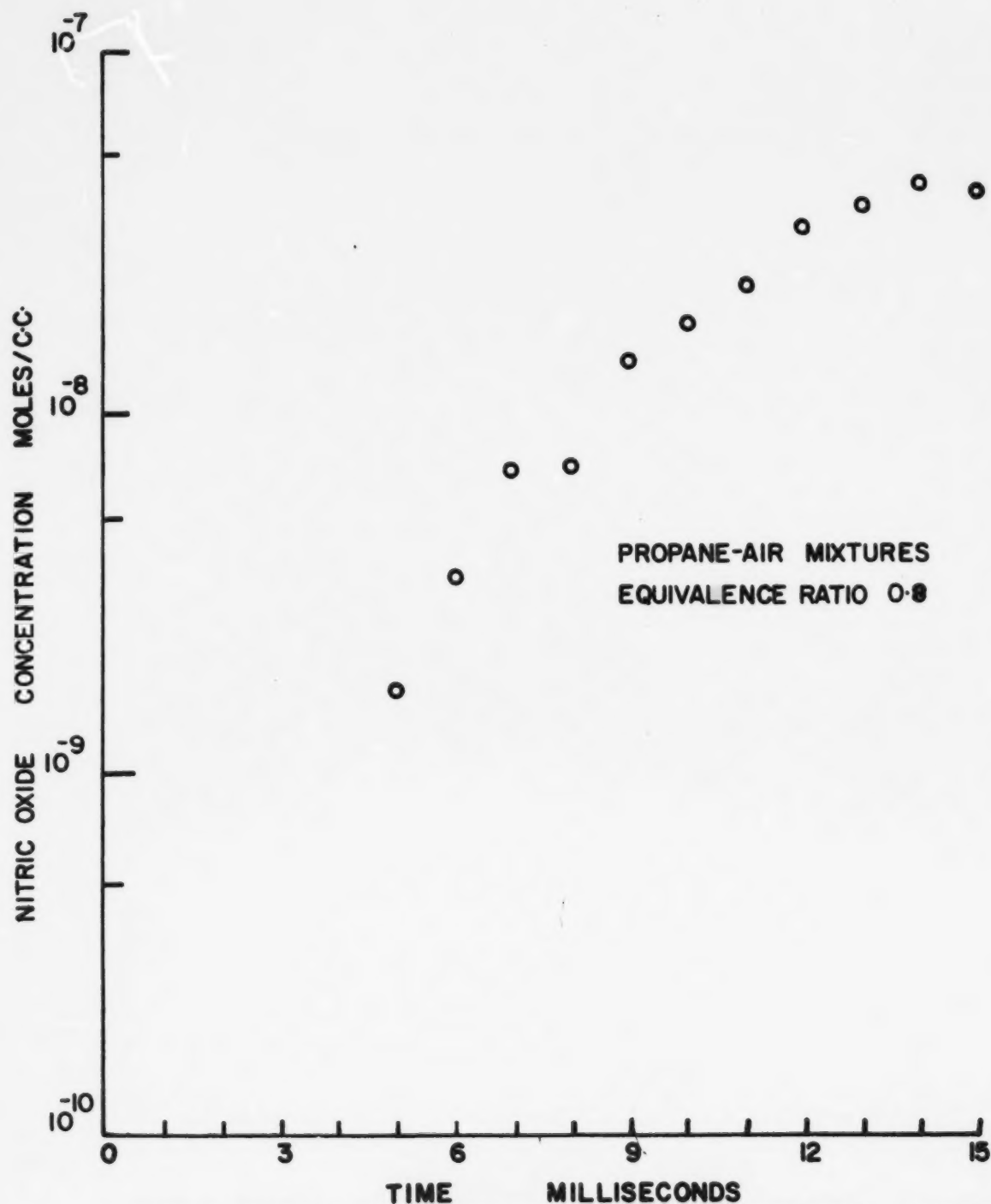
TIME MILLISECONDS
EXPERIMENTAL PRESSURE-TIME HISTORY

FIGURE 3-16

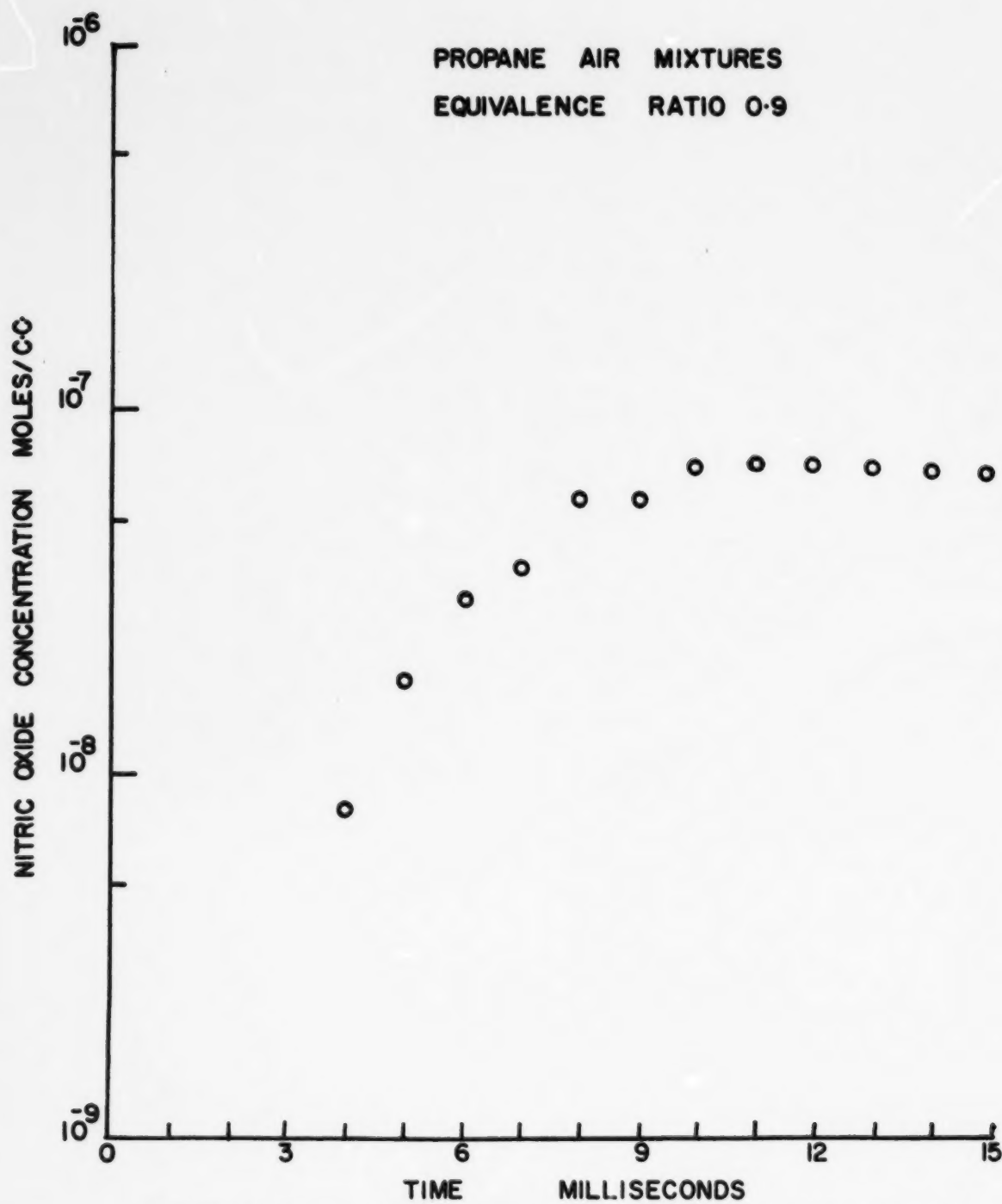


TIME MILLISECONDS
EXPERIMENTAL PRESSURE-TIME HISTORY

FIGURE 3-17

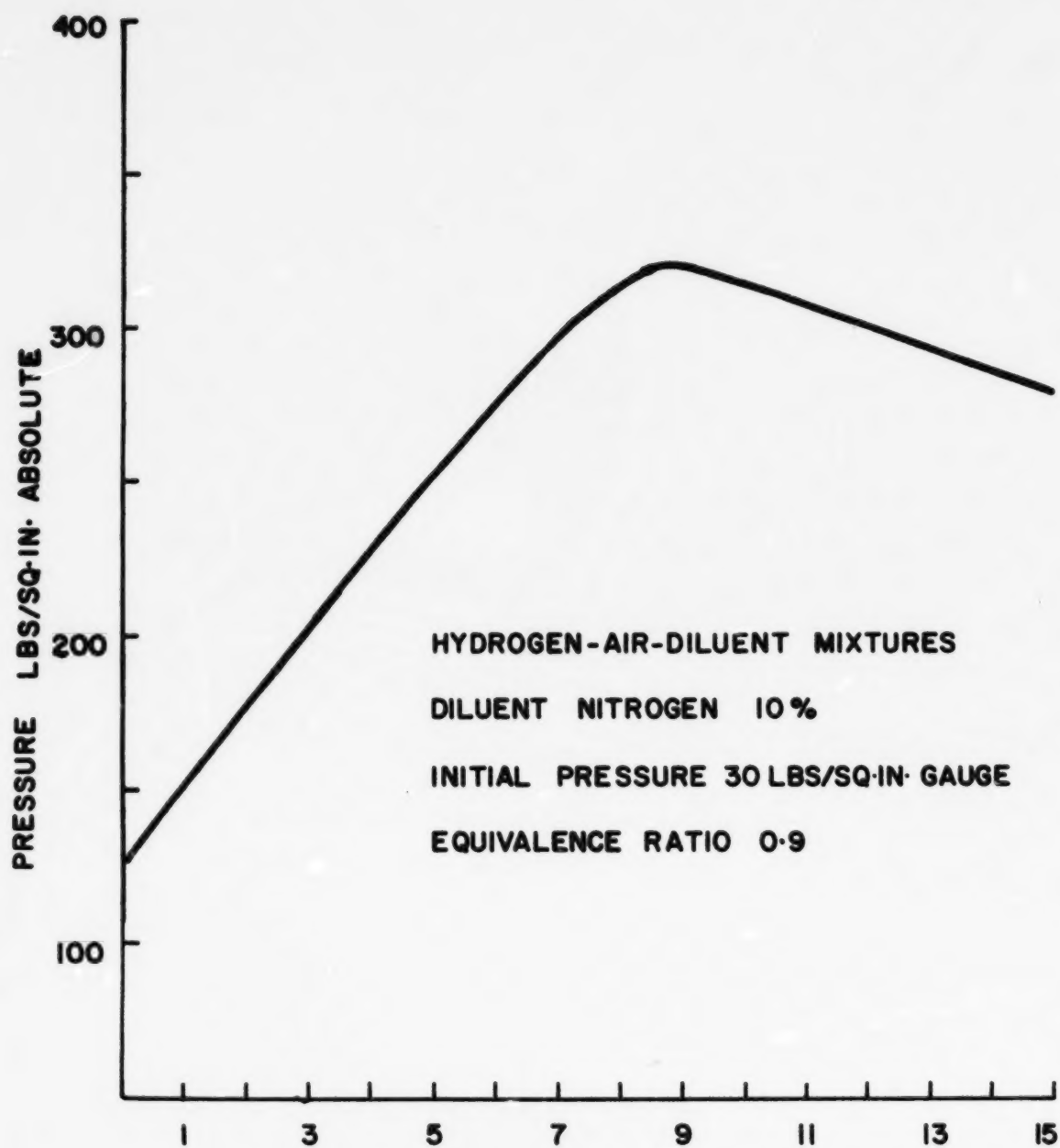


NITRIC OXIDE : EXPERIMENTAL CONCENTRATION-TIME HISTORY
FIGURE 3-18



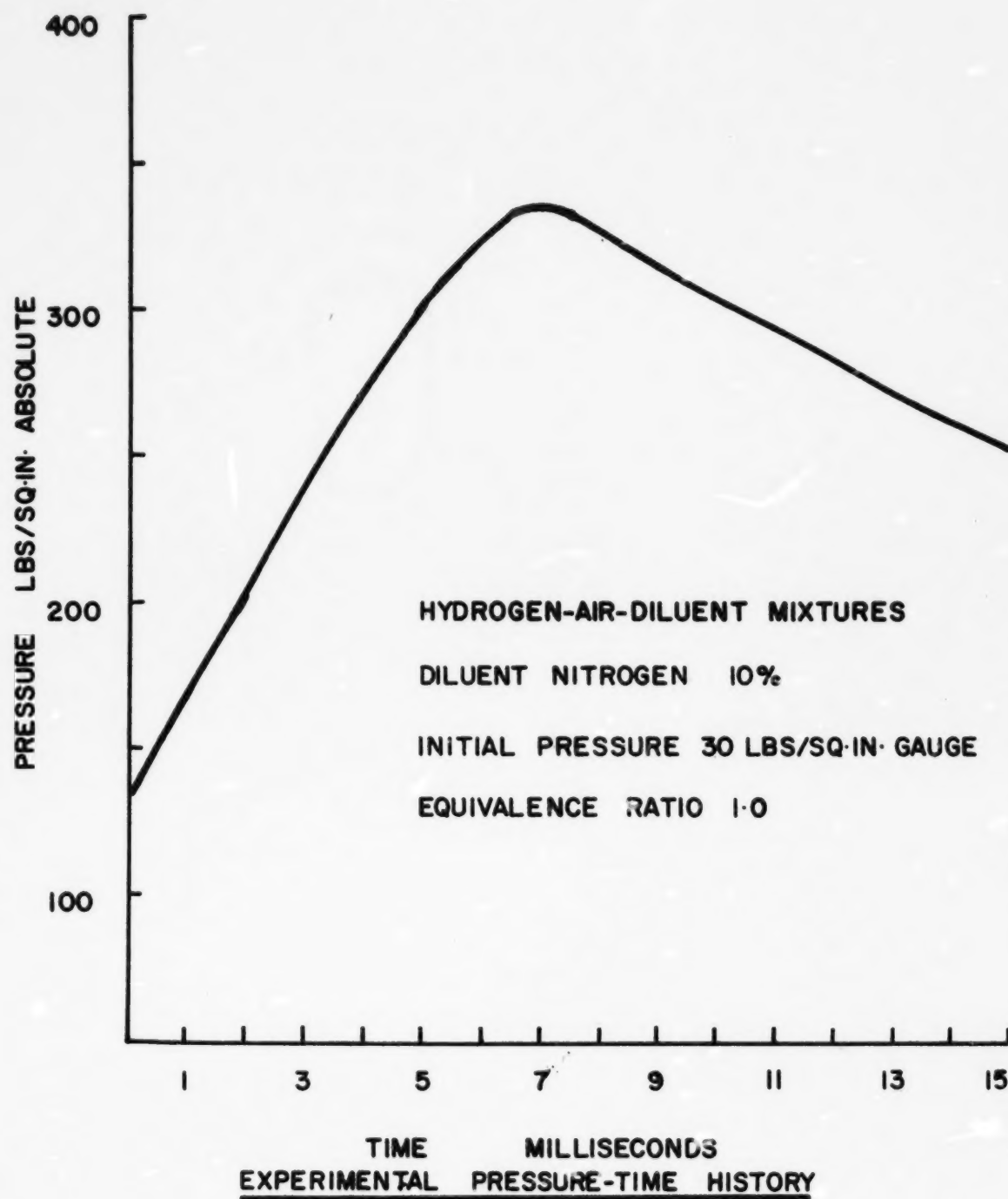
NITRIC OXIDE : EXPERIMENTAL CONCENTRATION-TIME HISTORY

FIGURE 3.19



TIME MILLISECONDS
EXPERIMENTAL PRESSURE-TIME HISTORY

FIGURE 3.20

FIGURE 3-21

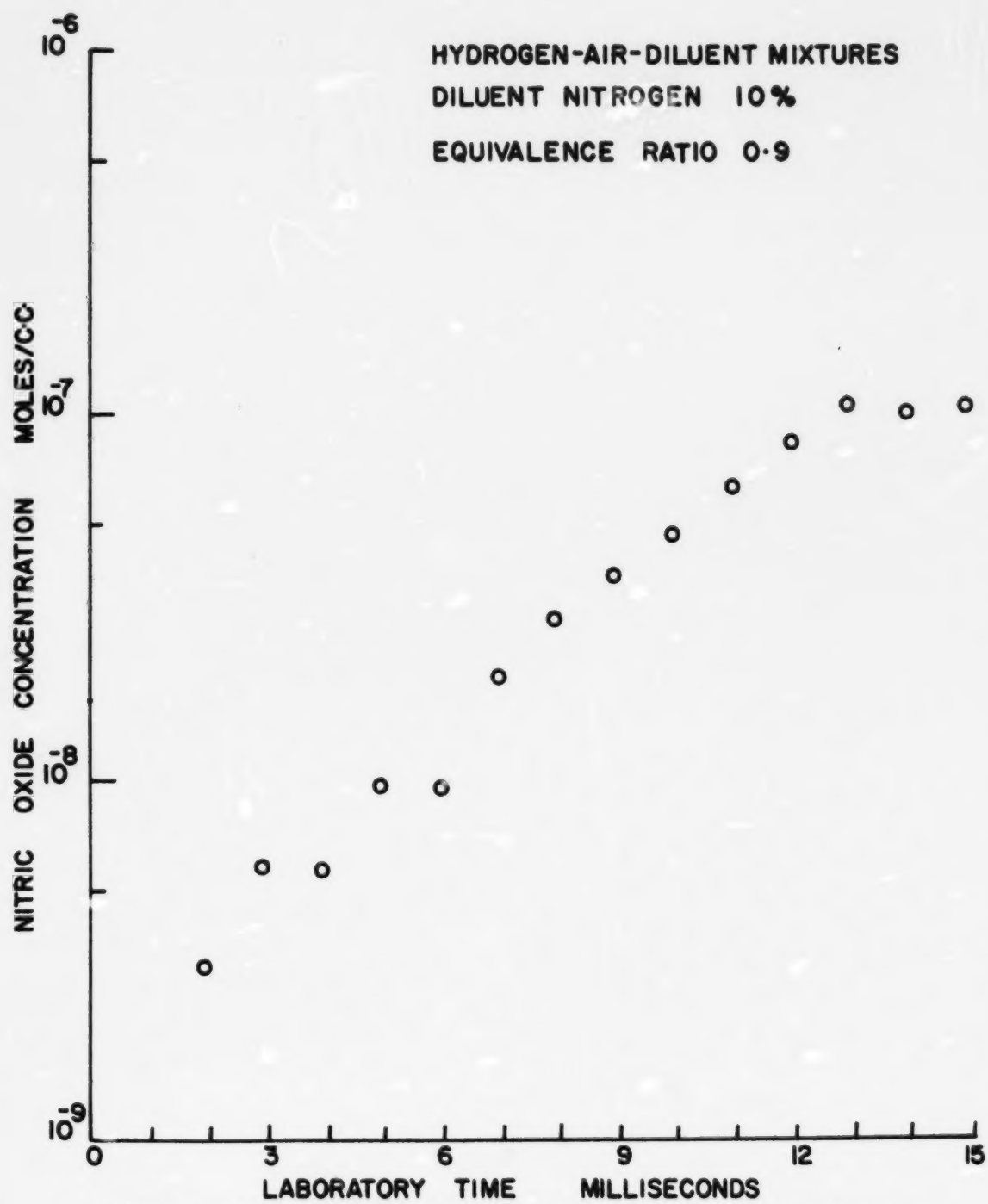
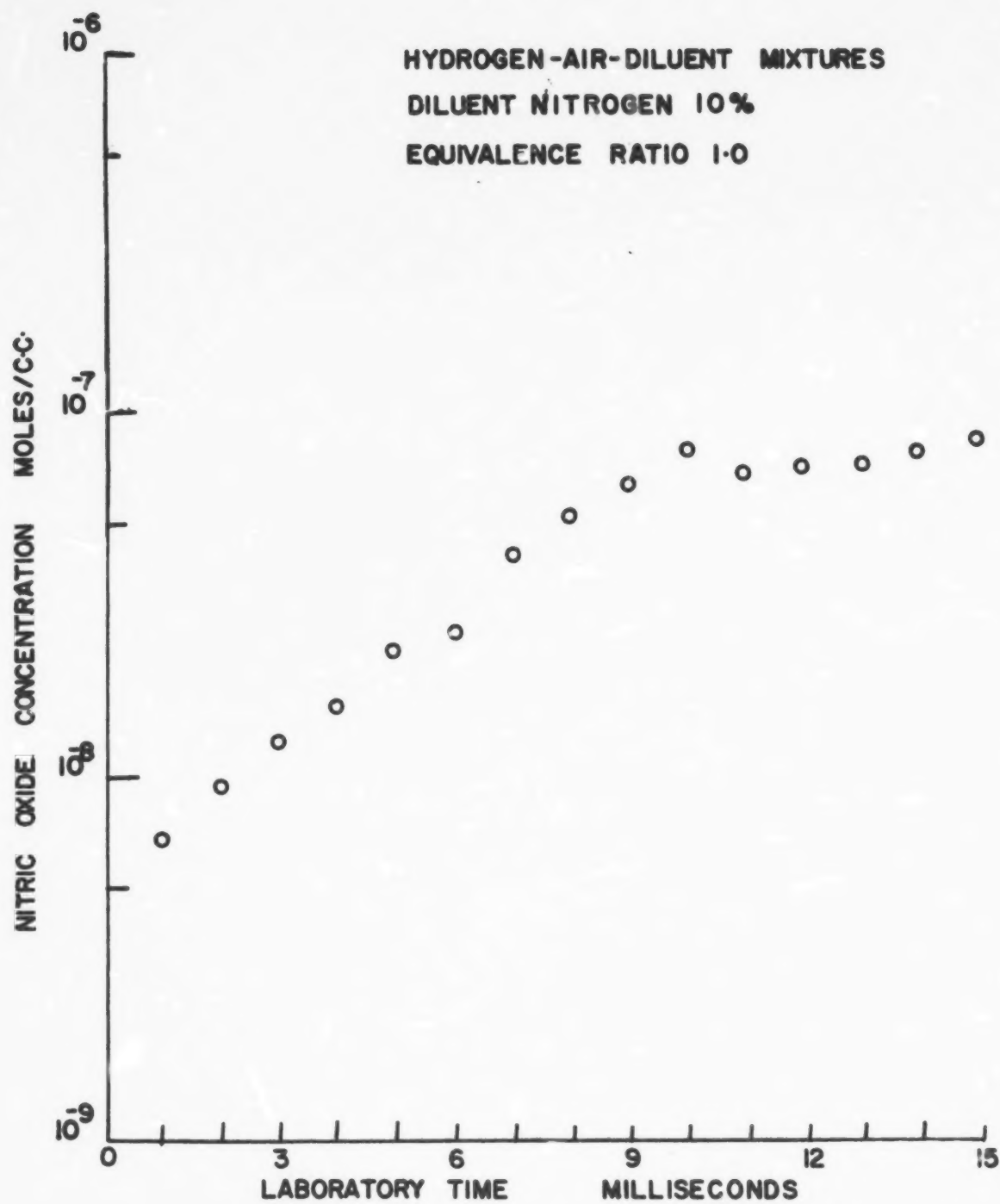


FIGURE 3-22



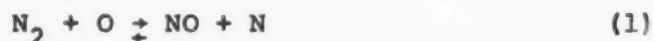
NITRIC OXIDE: EXPERIMENTAL CONCENTRATION-TIME HISTORY

FIGURE 3-23

CHAPTER IV THEORETICAL TECHNIQUES

4.1 Elementary Reactions

A reaction mechanism consisting of elementary chemical reactions has been used to predict the formation of nitric oxide. From a review of the literature it was found that the following elementary reactions are relevant to the formation and decomposition of nitric oxide.



The contributions of all reactions were examined closely and it was concluded that the only significant contribution to the formation of nitric oxide comes from reactions (1) and (2).

The reaction mechanism used, then, consists of only two elementary chemical reactions and is sufficient to predict the formation rates of nitric oxide in high pressure fuel-air mixtures.



The reaction rate constants employed in this work were obtained from the literature (52) and are presented in the table below

Reaction	Rate Constant mole/cm ³ -second
$N_2 + O \rightarrow NO + N$	$7 \times 10^{13} \exp(-75,500/RT)$
$NO + N \rightarrow N_2 + O$	1.55×10^{13}
$O_2 + N \rightarrow NO + O$	$13.3 \times 10^9 xT \exp(-7080/RT)$
$NO + O \rightarrow O_2 + N$	$3.2 \times 10^9 \exp(-39,100/RT)$

The proposed reaction mechanism leads to a single differential equation in $[NO]$, the concentration of nitric oxide. The solution of this equation requires knowledge of the instantaneous concentrations of atomic and molecular oxygen and nitrogen i.e. $[O]$, $[O_2]$, $[N]$ and $[N_2]$.

Experimental results presented in chapter III indicate that the formation of nitric oxide is slow relative to the probable rates of post flame relaxation of atoms and radicals to equilibrium concentration. Therefore chemical equilibrium concentrations of oxygen and nitrogen atoms and molecules corresponding to instantaneous post flame temperatures and pressures are employed in the solution of the differential equation.

Numerical evaluation of reaction rate constants and equilibrium species concentrations requires knowledge of the temperature and pressure of post flame gases. Equilibrium adiabatic flame temperatures based on measured pres-

tures are employed for this calculation. The use of equilibrium species concentrations and equilibrium temperatures is justified more fully in article 5.1. The calculation of these quantities is discussed in article 4.3.

4.2 Formation Kinetics

The reaction mechanism used for prediction of nitric oxide formation leads to a single first order differential equation

$$\frac{d[\text{NO}]}{dt} = k_{1f}[\text{N}_2][\text{O}] - k_{1b}[\text{NO}][\text{N}] + k_{2f}[\text{O}_2][\text{N}] - k_{2b}[\text{NO}][\text{O}] \quad 4.2-1$$

where, according to the usual convention, parentheses indicate concentration of the respective species in moles/c.c. and the k 's are the reaction rate constants of the reactions '1' and '2' in the forward 'f' and reverse 'b' directions.

Equation 4.2-1 is a nonlinear first order ordinary differential equation. This is solved numerically using a Runge Kutta technique of integration. From the experimentally measured pressure trace the instantaneous pressure is used to calculate the adiabatic flame temperature and equilibrium concentration of atomic and molecular oxygen and nitrogen. The substitution of the instantaneous values of temperature and species concentrations, $[\text{O}]$, $[\text{O}_2]$, $[\text{N}]$ and $[\text{N}_2]$ into the right hand side of equation 4.2-1 allows a stepwise integration for the concentration of nitric oxide, $[\text{NO}]$.

4.3 Adiabatic Flame Temperature and Equilibrium Species Concentration*

Equilibrium species concentrations for any fuel-air combination $C_w H_x O_y N_z$ is calculated using a previously developed computer program (38). The input to this program besides composition (w, x, y and z) and stoichiometric ratio, is the pressure and temperature of the system.

For adiabatic combustion process (at constant pressure) the following relation is satisfied

$$H|_{T_i, p}^{\text{reactants}} = H|_{T_{eq}, p}^{\text{products}} \quad 4.3-1$$

where

H is the absolute enthalpy

T_i is the initial temperature

T_{eq} is the equilibrium flame temperature

p is the system pressure.

Trial values of T_{eq} are used to calculate equilibrium species concentration using the previously developed program as a subroutine. This calculation gives the product composition for this trial value of equilibrium flame temperature. Using thermochemical data from the literature (22) the absolute enthalpies on the right and left hand sides of equation 4.3-1 are calculated. The trial value of T_{eq} is adjusted until the two enthalpy values match.

*The initial development of this calculation was done by Arjun Dev Tuteja of the Department of Mechanical Engineering, University of Wisconsin.

4.4 Effect of Convective Motion--Time Correction Procedure

The effect of convective motion is illustrated by considering the following sequence of events in conjunction with figure 4.1. Here, the flame originating at $x = 0$ propagates to the right. Due to thermal expansion as the reactants are consumed by the flame front, previously burned combustion products behind the flame front are compressed, and a one dimensional convective motion from right to left results.

At time $t = 0$ the flame reaches the optical path, located at the fixed position x^* , and time measurement begins. At a later time $t = \tau$, the flame reaches a point $x_f(\tau) > x^*$. At a still later time $t = t$, products formed at x_f and τ have been compressed back to the optical path at point $x = x^*$. For the spectroscopic observation made at this instant, the time of interest kinetically is not the total recorded time, t , but rather the time difference $(t - \tau)$ which represents the time elapsed between inflammation and spectroscopic observation of the products observed by the spectrometer.

The motion of combustion products behind the flame front can be represented by a velocity field $u(x,t)$. Then the local motion of products in a differential time dt , is given

$$dx = u(x,t) dt \qquad 4.4-1$$

For the one dimensional system represented by

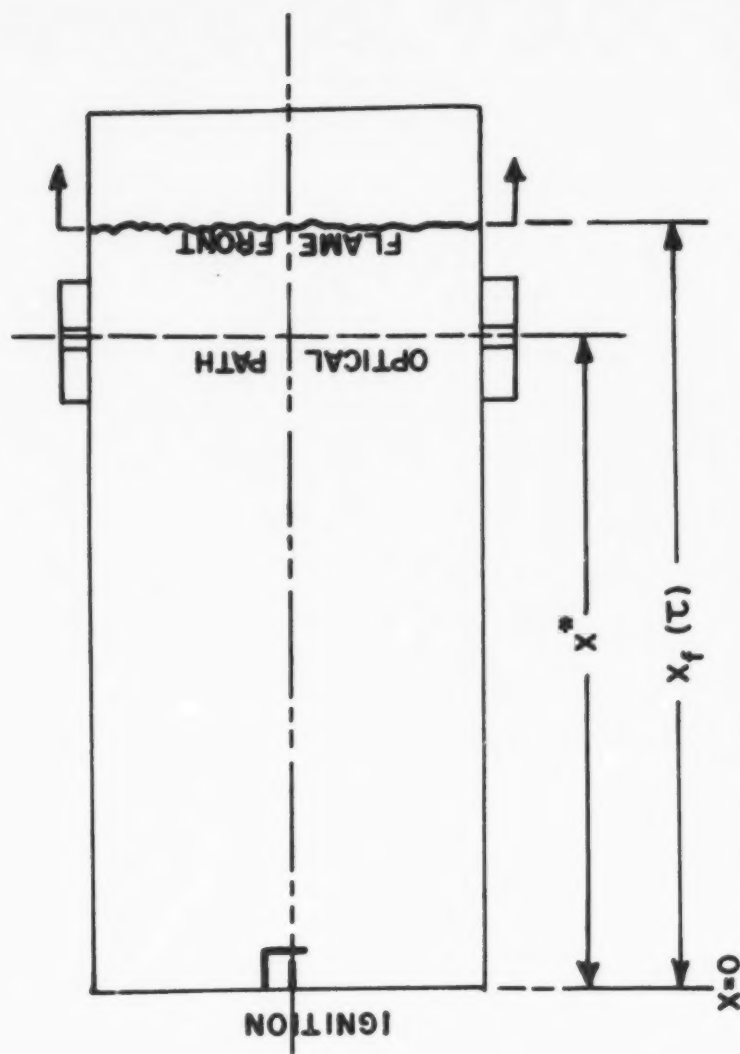


ILLUSTRATION FOR EVALUATION OF TIME SCALE CORRECTION

FIGURE 4-1

by figure 4.1 the continuity equation takes the form

$$\frac{\partial \rho}{\partial t} = -\rho \frac{\partial u}{\partial x} - u \frac{\partial \rho}{\partial x}$$

Assuming that pressure is uniform within the system and the temperature of combustion products is nearly uniform, the above partial differential equation reduces to the ordinary equation

$$\frac{d\rho}{dt} = -\rho \frac{du}{dx}$$

Because the velocity, $u(0,t)$, at the left hand boundary must be zero, integration of the above equation yields the result

$$\int_0^{u(x,t)} du = - \int_0^x \frac{1}{\rho(t)} \frac{d\rho}{dt} dx$$

or,

$$u(x,t) = -\frac{1}{\rho} \frac{d\rho}{dt} x \quad 4.4-2$$

For isentropic behavior of post flame combustion products,

$$\frac{d\rho}{\rho} = \frac{1}{\gamma} \frac{dp}{p}$$

Substitution into equation 4.4-2 yields the result,

$$u(x,t) = -\frac{1}{\gamma p(t)} \frac{dp}{dt} x \quad 4.4-3$$

Thus the instantaneous velocity field of combustion products $u(x,t)$, is expressed solely as a function of the experimentally measured pressure and the position x .

Substituting this result into equation 4.4-1. the

resulting differential equation for the motion of combustion products is,

$$dx = -\frac{x}{\gamma p} \frac{dp}{dt} dt$$

Separating variables and integrating from time when reactants at position at x_f are consumed by the flame to time t , when the resulting products reach the optical path,

$$\int_{x_f}^x \frac{dx}{x} = - \int_t^{\tau} \frac{1}{\gamma p} \frac{dp}{dt} dt$$

and

$$\ln \frac{x_f}{x} = \frac{1}{\gamma} \ln \frac{p(t)}{p(\tau)} \quad 4.4-4$$

Equation 4.4-4 is used directly in conjunction with the experimentally measured pressure recordings to obtain the corrected kinetic time, $(t-\tau)$ corresponding to each instant of observation.

For a given time the pressure $p(\tau)$ is evaluated from the pressure trace. The corresponding flame location $x_f(\tau)$ is evaluated by a thermodynamic calculation based on the equation

$$x_f = \frac{\ell \left(\frac{p}{p_i} \right)^{\frac{-1}{\gamma_u}} - 1}{\frac{T_i}{T_b} \left(\frac{p}{p_i} \right)^{\frac{\gamma_u}{\gamma_u - 1}} - 1} \quad 4.4-5$$

Equation 4.4-5 is simply derived from thermodynamic considerations. The details of the derivation are given in Appendix A. With these values of $p(\tau)$ and $x_f(\tau)$ equation 4.4-4 can be solved for $p(t)$. τ , then represents the instant of inflammation of sample of reactants at position x_f and t represents the instant of spectroscopic observation of the resulting products. The kinetic time or the effective time of nitric oxide formation in post flame gases is then the time difference $(t - \tau)$. The value of t is obtained by re-entering the pressure trace with this value of $p(t)$. This process is repeated for various selected values of τ .

It is readily seen that this correction for convective motion is carried on until $p(t)$ equals the maximum recorded pressure. Beyond this time all convective motion ceases and the sample of combustion products corresponding to the condition $p(t)$ equals maximum pressure continues to sit in the optical path.

4.5 Integration Procedure:

The reaction mechanism used leads to a single first order differential equation -- 4.2-1

$$\frac{d[\text{NO}]}{dt} = K_{1f}[\text{N}_2][\text{O}] - K_{1b}[\text{NO}][\text{N}] + K_{2f}[\text{O}_2][\text{N}] - K_{2b}[\text{NO}][\text{O}] \quad 4.2-1$$

The solution of this equation gives the theoretically calculated concentration-time history of nitric oxide

to be compared with experimentally measured values presented in article 3.6.

Equation 4.2-1 is integrated numerically using shifting equilibrium concentrations of O, O₂, N and N₂. The effect of flame propagation as discussed in article 4.4 is also taken into consideration.

A computer program has been developed for use on the UNIVAC 1108. The schematic flow chart and the general description of the program are given in this section and the program listing is included in Appendix B.

The equilibrium species distribution program mentioned in article 4.3 is used in the form of two subroutines SPECY1 and SPECY2, one for lean and chemically correct mixtures and the other for rich mixtures. The subroutines give the equilibrium concentration of eleven major species for a specified fuel-air composition at a specified pressure and temperature.

The computer program developed for the present calculation requires an input of

- (1) the pressure trace (coefficients of the pressure time polynomial fitted to experimentally measured pressure values).
- (2) fuel composition, stoichiometric air, stoichiometric ratio and number of moles of diluent per mole of fuel.
- (3) properties of fuel i.e. the enthalpy of formation

at 298°K and polynomial coefficients of C_p (specific heat at constant pressure) as a function of temperature.

(4) properties of burnt and unburnt gases i.e. γ_b , γ_u the ratios of specific heats.

The program computes the concentration of nitric oxide in the optical path at any instant of time. This instant of time is selected at suitable intervals by means of a DO LOOP.

At the selected instant τ , the program computes x_f , the position of the flame front. This instant marks the inflammation of the gas sample at position x_f . At this instant of time which is kinetically zero time for this parcel of mass the concentrations of O, O_2 , N and N_2 are set equal to their respective equilibrium concentrations while the concentration of nitric oxide is set equal to zero, since nitric oxide formation is a post flame phenomenon as determined experimentally. This sample of gas is compressed back to the optical path at the instant 't'. The value of 't' is calculated through the use of equation 4.4-4 and the experimental pressure trace as outlined in article 4.4.

The kinetic time of nitric oxide formation of this parcel of gas is then the difference in time between the instants of inflammation and spectroscopic observations i.e. $(t - \tau)$. The formation of nitric oxide in this parcel during this interval of time is given by equation 4.2-1. The program integrates this equation from

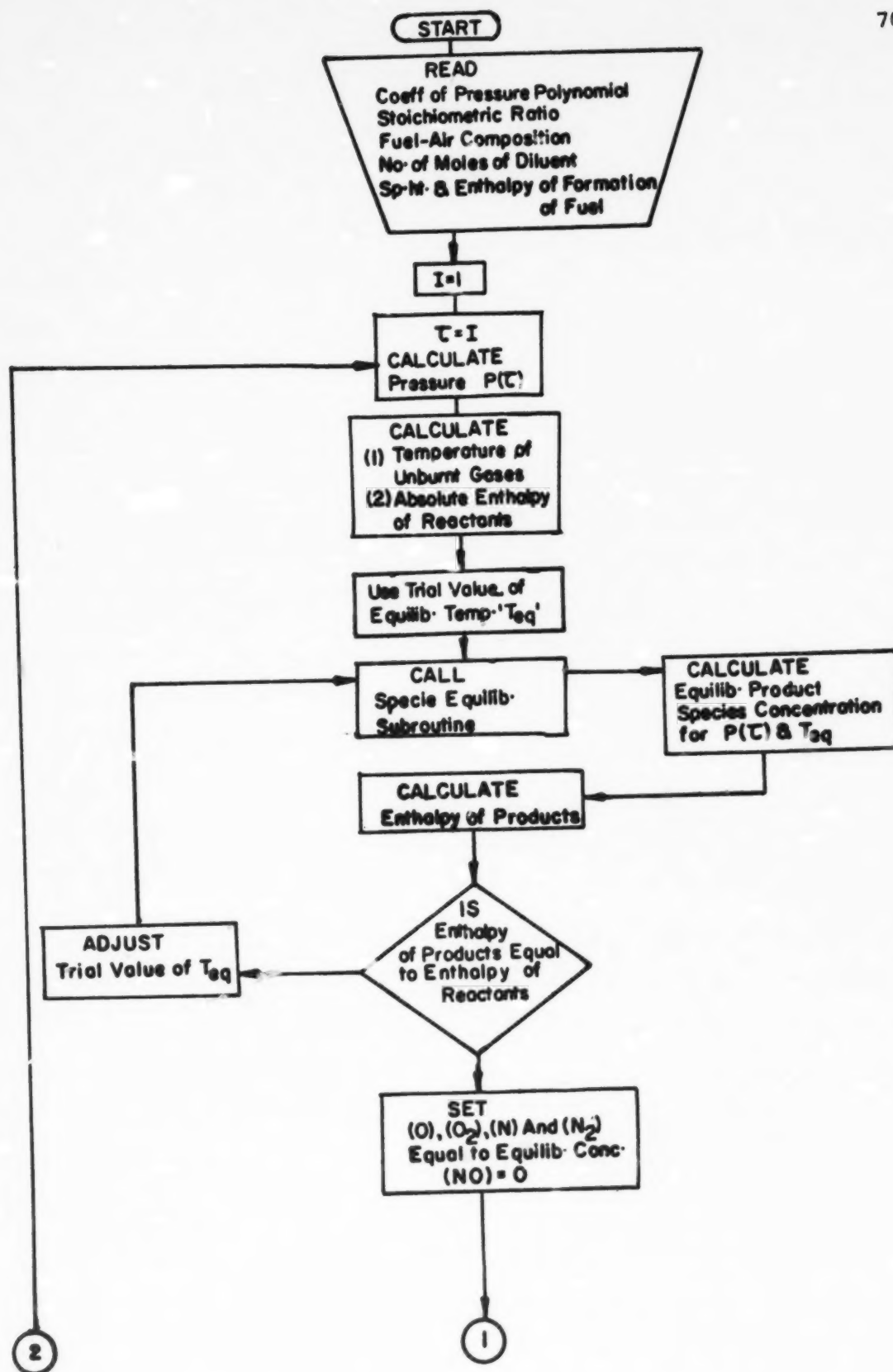
kinetic time zero to kinetic time ($t - \tau$). The integration is performed by a stepwise Runge Kutta process using shifting equilibrium concentrations of O, O₂, N and N₂ corresponding to shifting pressure and temperature at each step of integration. The pressure at each step of integration is given by the measured pressure trace while the temperature is calculated using the isentropic compression relationship given in equation 4.5-1.

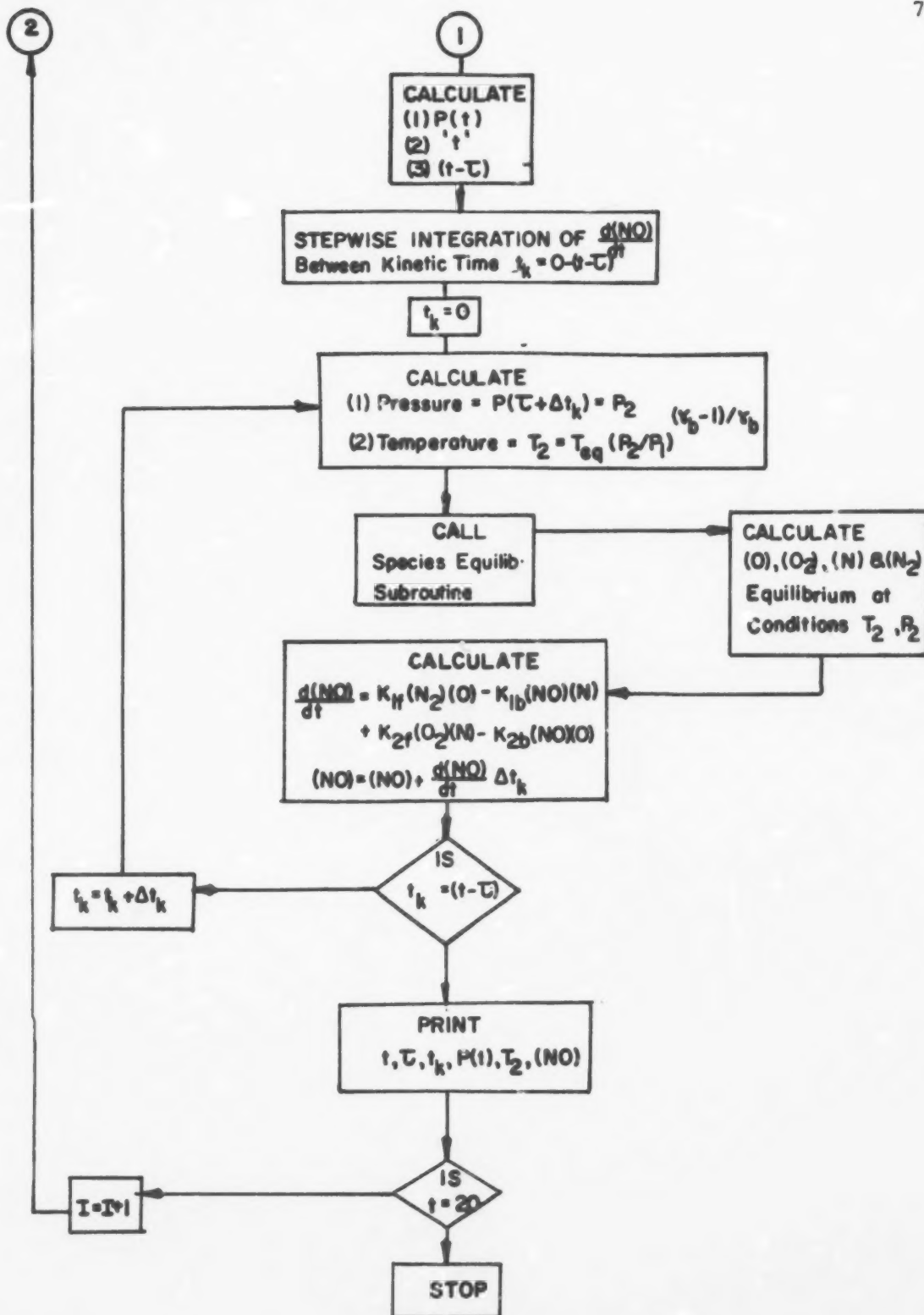
$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{\frac{\gamma_b - 1}{\gamma_b}} \quad 4.5-1$$

At the end of this stepwise integration the result of the calculation represents the concentration of nitric oxide in the optical path at the instant 't'. The DO LOOP then repeats this calculation for a series of times τ , so that the concentration of nitric oxide in the optical path as a function of measured time 't' is ultimately obtained.

Further, at the end of combustion as defined by the point of peak pressure, all convective motion of gas is assumed to cease. The last sample of combustion products then remains in the optical path. The kinetic integration for the formation of nitric oxide can then be extended beyond this point without further corrections in measured time.

The results of this calculation are plotted as solid





lines in figures 5.1 thru 5.9 for hydrogen-air mixtures. It is evident that there is an excellent agreement between theory and experiment.

4.6 Treatment of Propane:

The mechanism of formation of nitric oxide in propane-air mixtures appears to be kinetically identical to the mechanism of formation in hydrogen-air mixtures. This is due to the fact that nitric oxide formation occurs predominantly in the post flame gases. In this region all combustion reactions are complete and there is no chemical specificity of the fuel.

Experimentally measured pressure traces for propane-air mixtures are shown in figures 3.16 and 3.17 for equivalence ratios 0.8 and 0.9. The corresponding pressure traces for hydrogen-air mixtures are shown in figures 3.7 and 3.8. A comparison of the pressure traces clearly indicates that during the time of measurement the pressure in propane-air mixtures remains essentially constant. This is due to the fact that the rate of the flame propagation in hydrogen-air mixtures is greater than that in propane-air mixture by a factor of about 8 to 10. Thus, while the flame propagation process in hydrogen-air mixtures may be regarded as essentially adiabatic, this assumption does not hold in the case of propane-air mixtures. The combined effect of heat transfer and flame propagation keep the pressure nearly

constant during the interval of measurement considered. Hence the formation process of nitric oxide during this interval of time may be regarded as a constant pressure process.

Accordingly a straightforward calculation at this constant pressure gives the equilibrium species concentrations and the equilibrium flame temperature, which may be regarded as constant during nitric oxide formation. Equation 4.2-1 then reduces to a linear first order differential equation with constant coefficients of the form

$$\frac{d[\text{NO}]}{dt} + A[\text{NO}] = B \quad 4.6-1$$

where $A = K_{1b}[\text{N}] + K_{2b}[\text{O}]$

$$B = K_{1f}[\text{O}][\text{N}_2] + K_{2f}[\text{N}][\text{O}_2]$$

Equation 4.6-1 can then be integrated in the closed form to give the solution

$$[\text{NO}] = B/A(1 - \exp(-At)) \quad 4.6-2$$

The initial condition used for the solution 4.6-2 is that at $t=0$ the concentration of nitric oxide (NO) = 0. The results of this calculation are plotted as solid lines in figures 5.6 and 5.7. As in the case of hydrogen the agreement between theory and experiment is excellent.

The same kinetic mechanism then predicts the formation of nitric oxide in both hydrogen-air and propane-air flames.

CHAPTER V RESULTS AND DISCUSSION

5.1 Presentation of Results:

Experimental results are presented in article 3.6. Using the method described in chapter IV the proposed reaction mechanism is used to theoretically predict the formation of nitric oxide. The results of these theoretical calculations are compared with the experimentally measured concentration time histories. This comparison is presented in figures 5.1 thru 5.5, where nitric oxide concentration is plotted against time. Solid lines represent the results of theoretical calculations discussed in chapter IV and experimental data points are reproduced from figures 3.11 thru 3.15. These figures represent the results of the following experimental conditions;

Fuel - Hydrogen

Diluent - O₂

Total initial pressure - 30 lbs./sq. inch gauge

Equivalence ratio - Indicated on each figure

Pressure traces corresponding to each of the above conditions are presented in figures 3.6 thru 3.10.

Figures 5.6 and 5.7 show similiar results for propane-air mixtures. Pressure traces for these conditions are presented in figures 3.16 and 3.17. Comparison of the pressure traces of hydrogen-air (3.7 and 3.8) and

propane-air (3.16 and 3.17) mixtures under similar conditions indicates that the slightly different treatment of propane outlined in article 4.6 is more than justified.

Figures 5.8 and 5.9 show the results of theoretical calculations and experimental measurements for hydrogen-air mixtures diluted with an inert diluent, in this case nitrogen. The experimental conditions are

Fuel - Hydrogen

Diluent - Nitrogen, 10%

Total initial pressure - 30 lbs./ sq. inch gauge

Equivalence Ratio - 0.9 and 1.0

Figures 3.20 and 3.21 show the corresponding pressure traces.

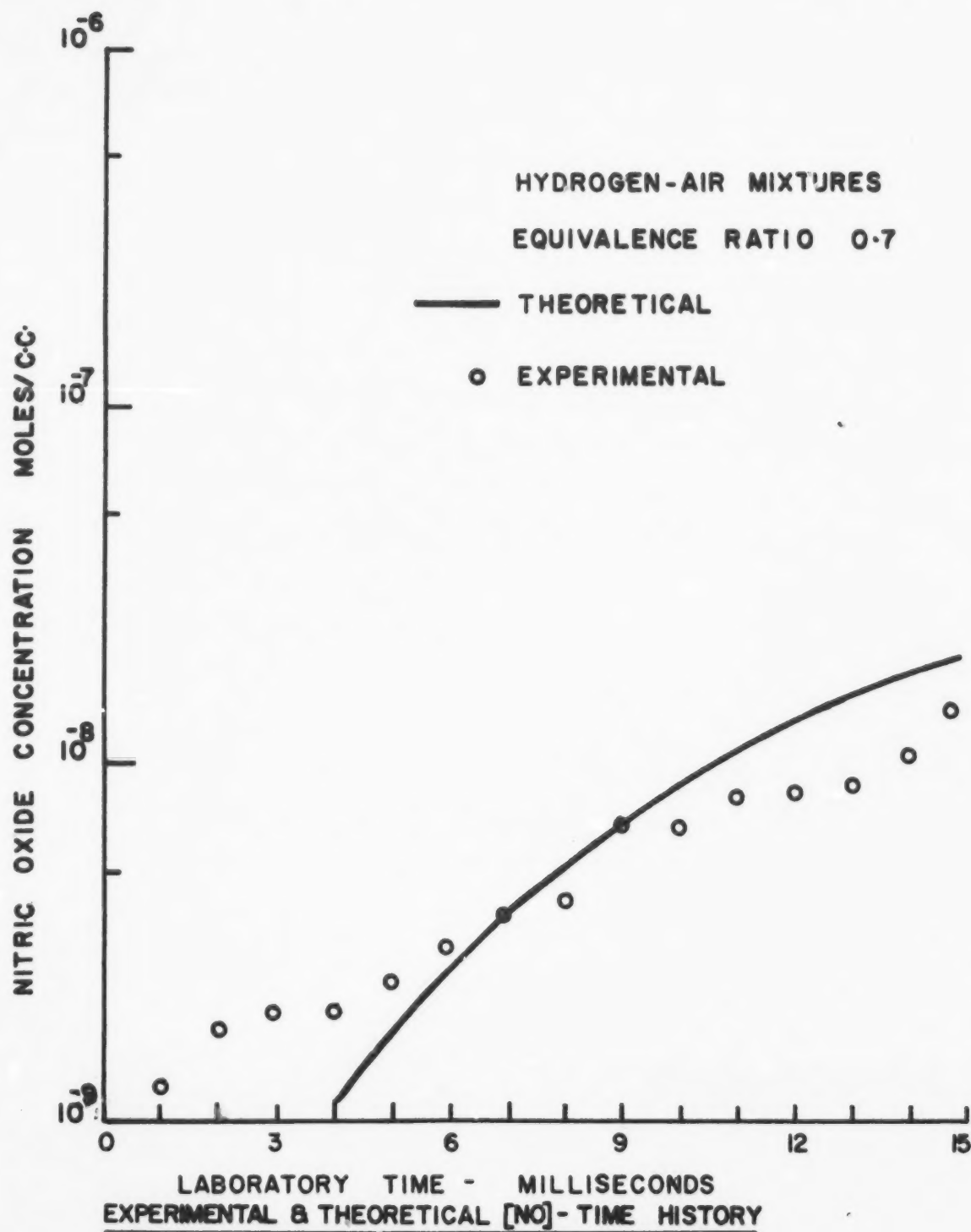
5.2 Discussion of Assumptions

Two major assumptions are made in using the proposed reaction mechanism. They are

(1) The concentrations of molecular and atomic oxygen and nitrogen i.e. $[O_2]$, $[O]$, $[N]$ and $[N_2]$ in the post flame gases is equal to equilibrium concentration corresponding to the instantaneous temperature and pressure of burnt gases.

(2) The temperature of burnt gases is equal to the adiabatic flame temperature.

In order to justify the first of these assumptions a number of theoretical studies were carried out. The hydrogen-air flame is studied in detail.

FIGURE 5-6

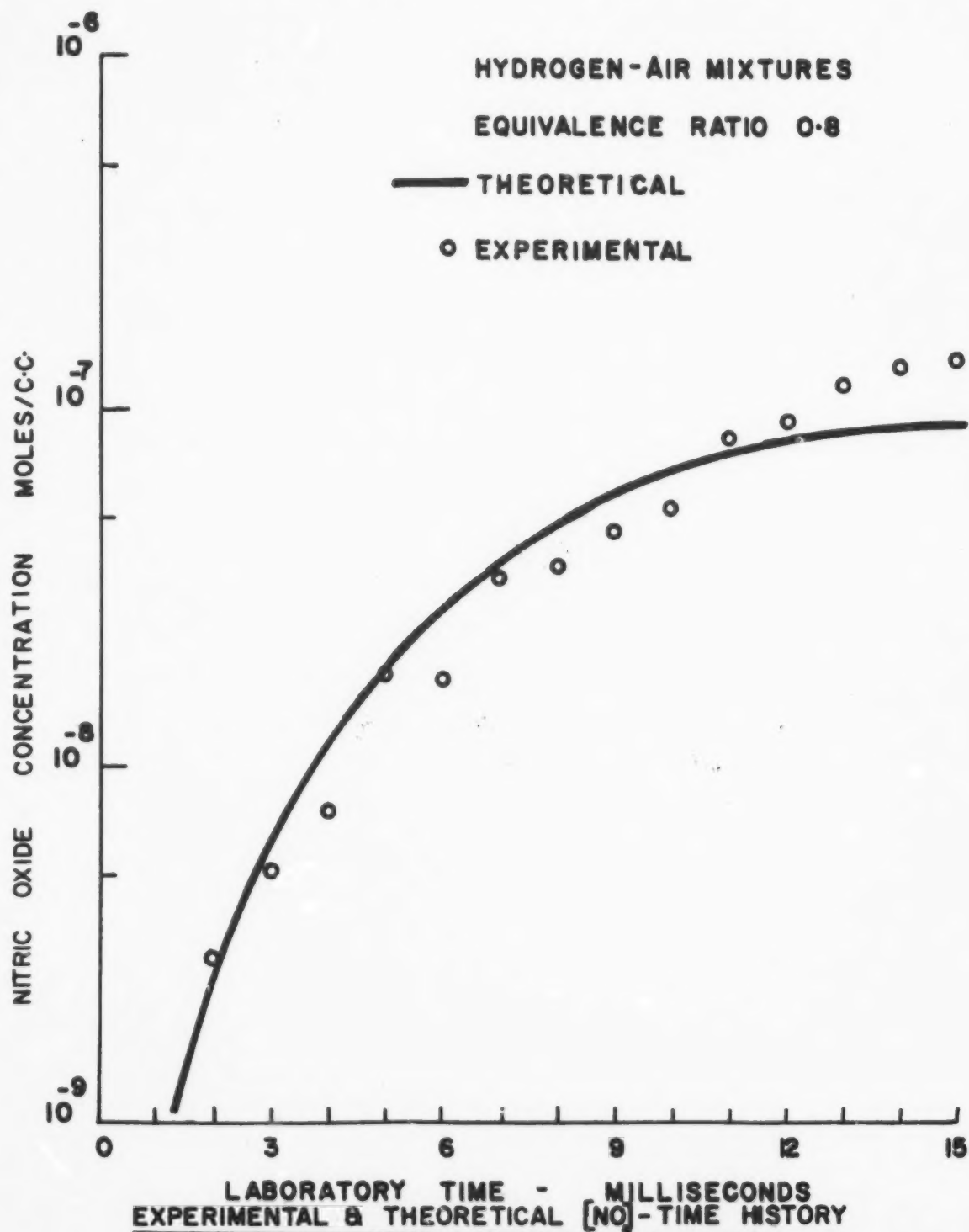
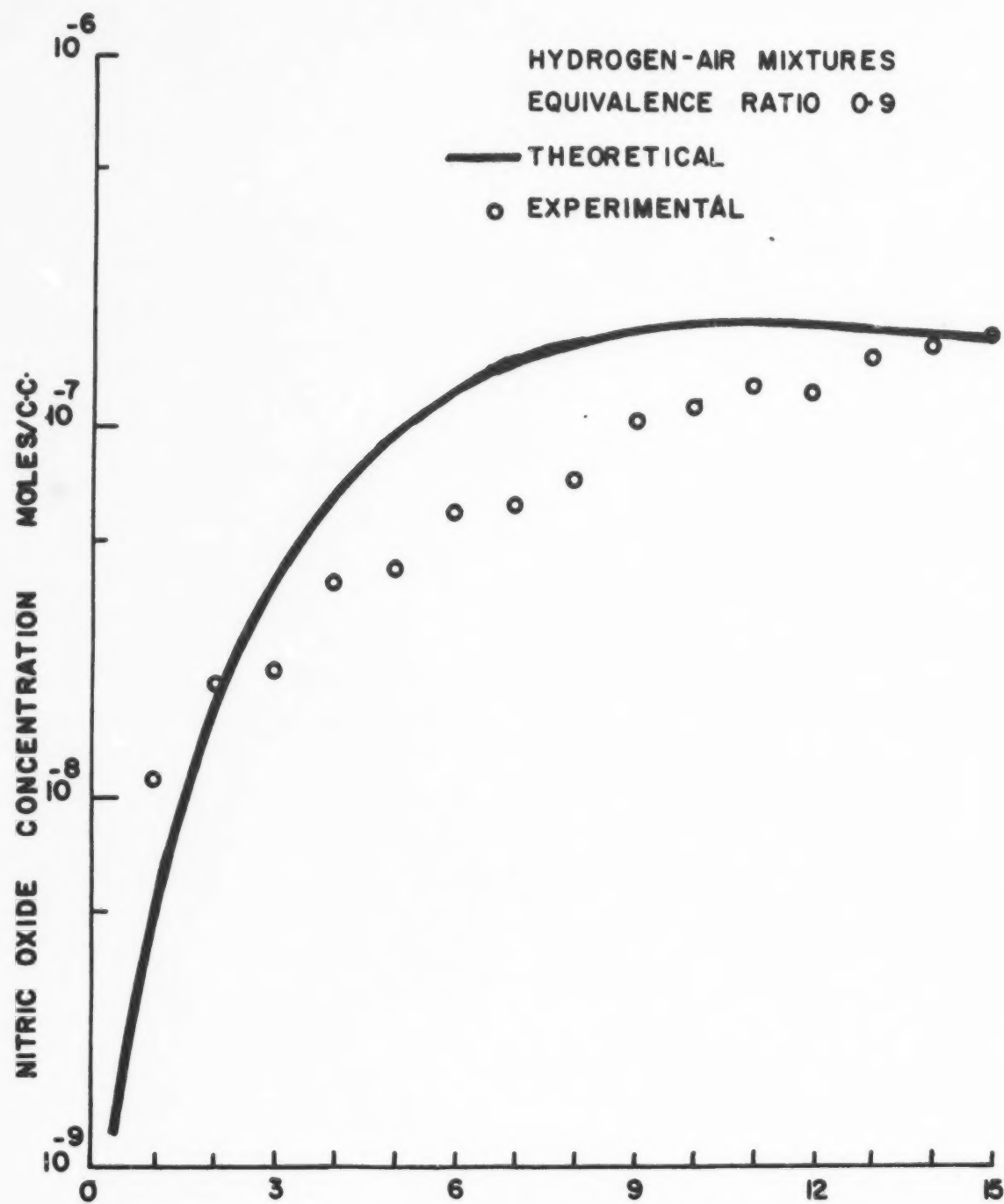


FIGURE 5-1



LABORATORY TIME - MILLISECONDS
EXPERIMENTAL & THEORETICAL [NO]-TIME HISTORY

FIGURE 5.3

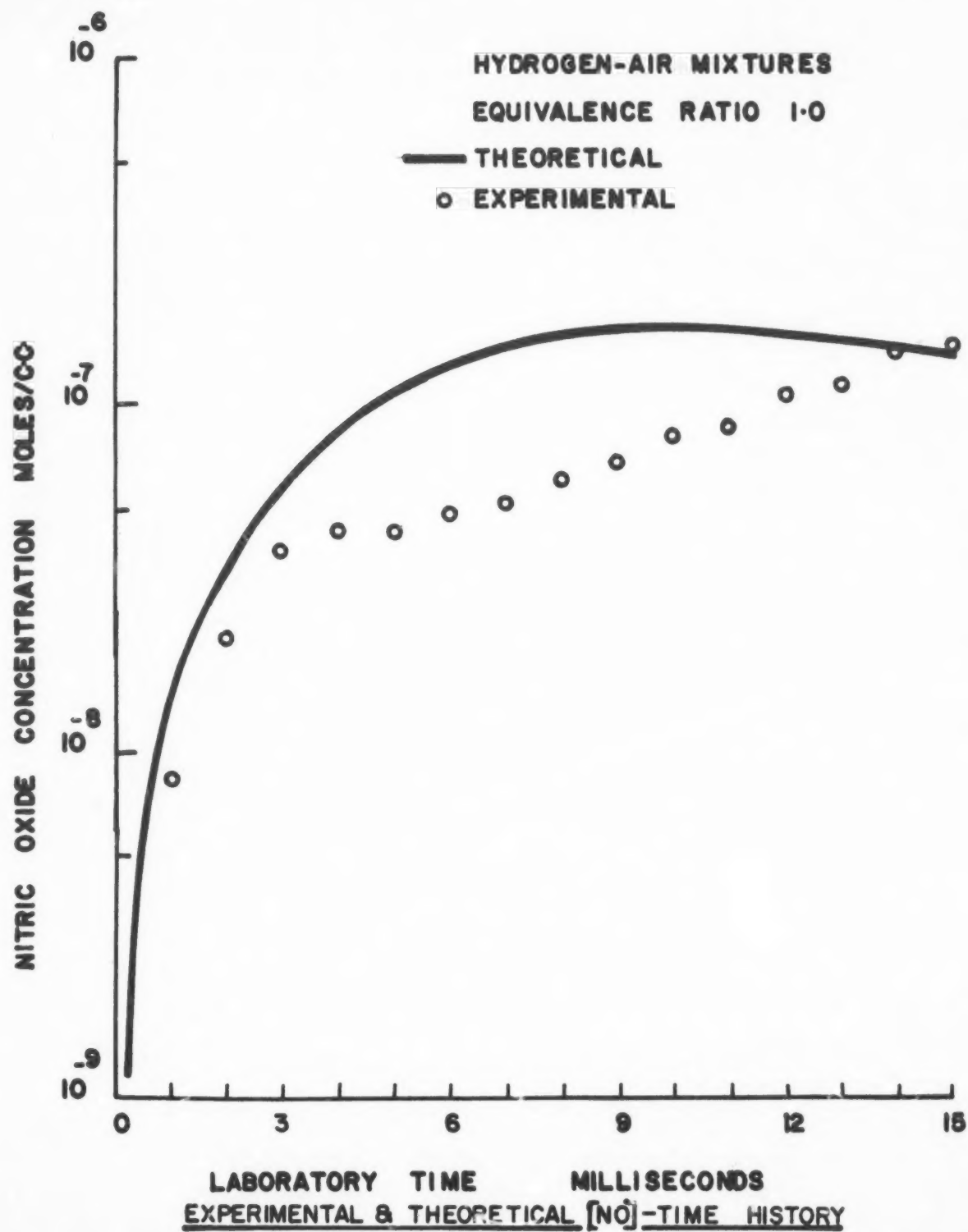


FIGURE 5.4

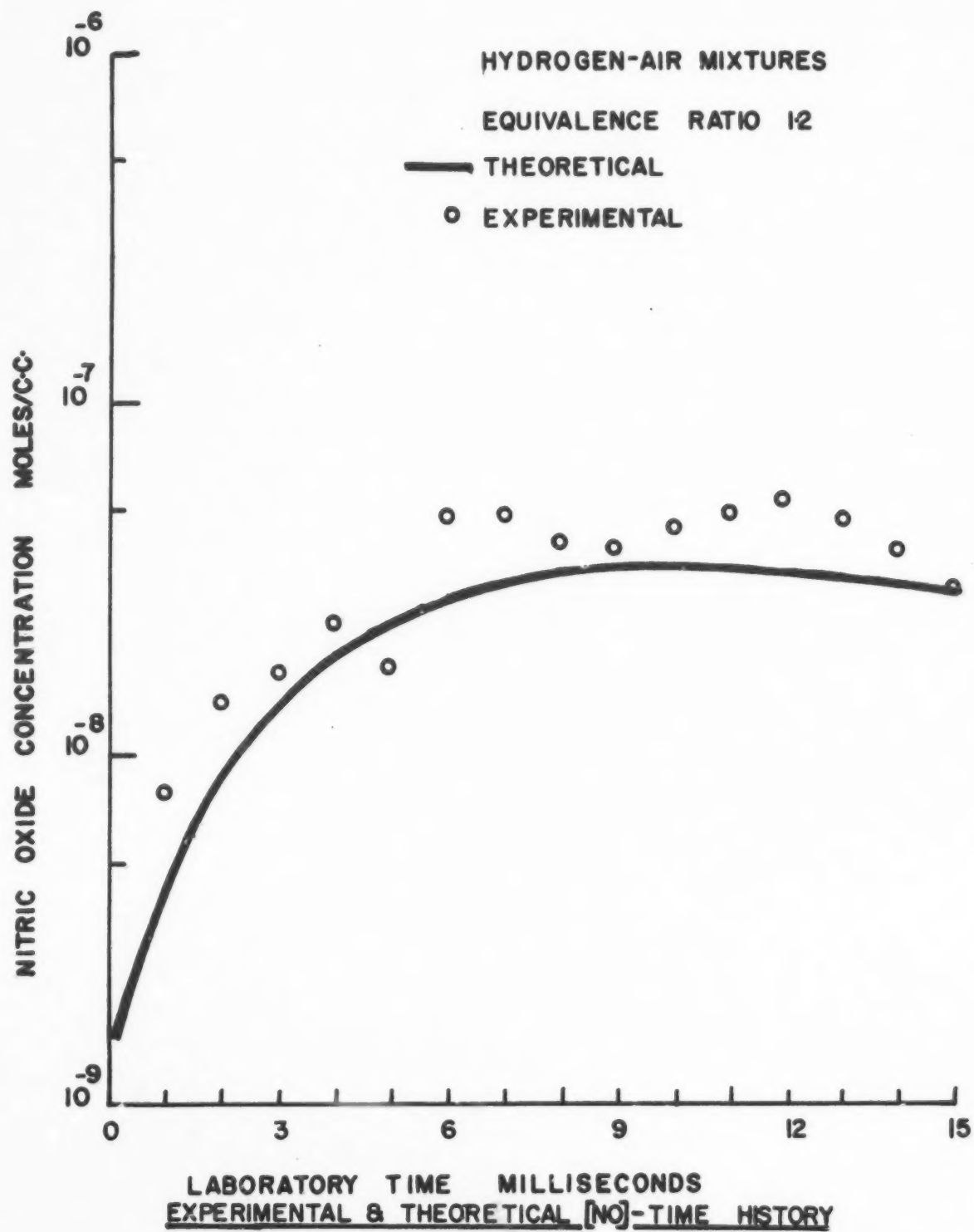


FIGURE 5-5

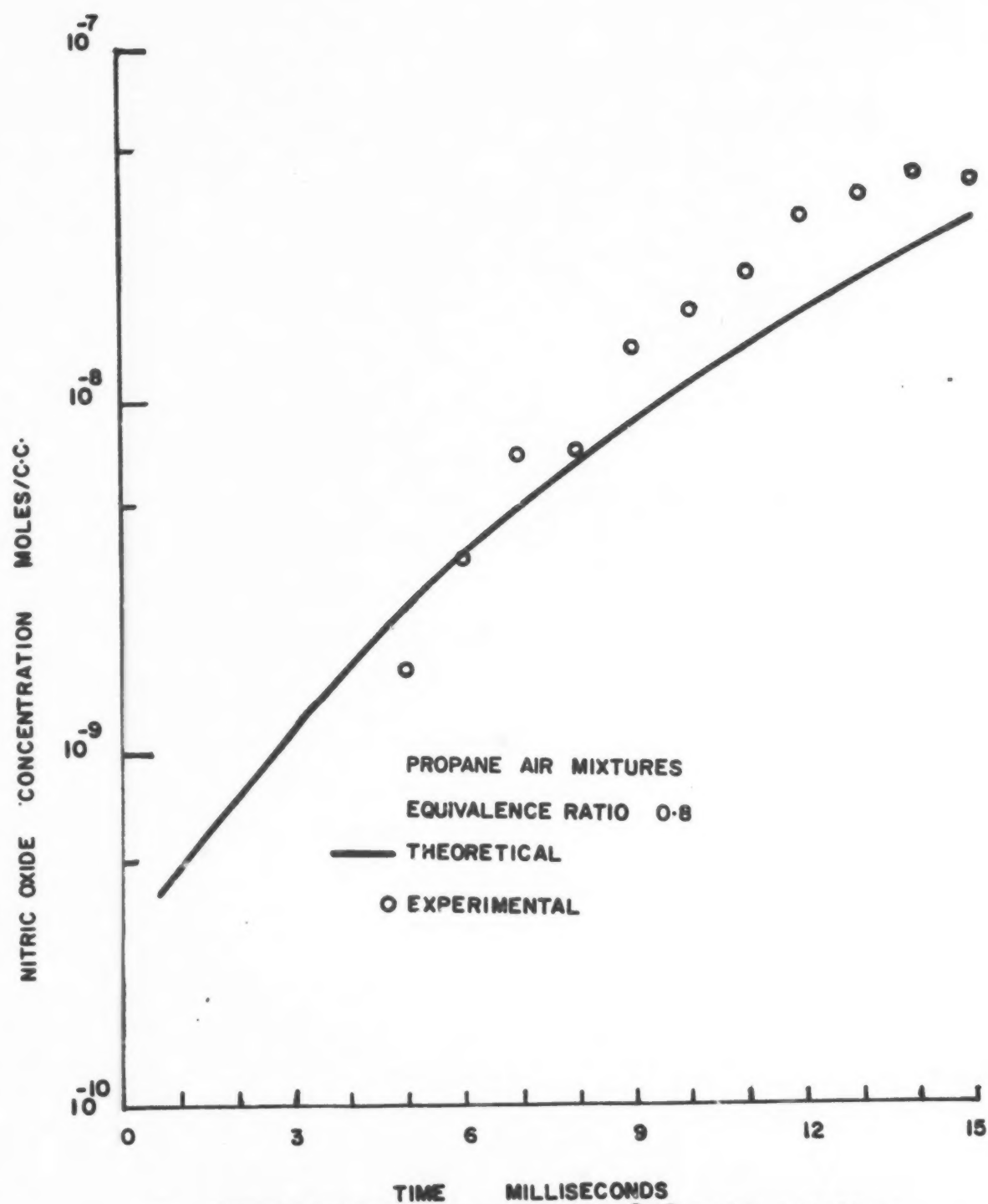
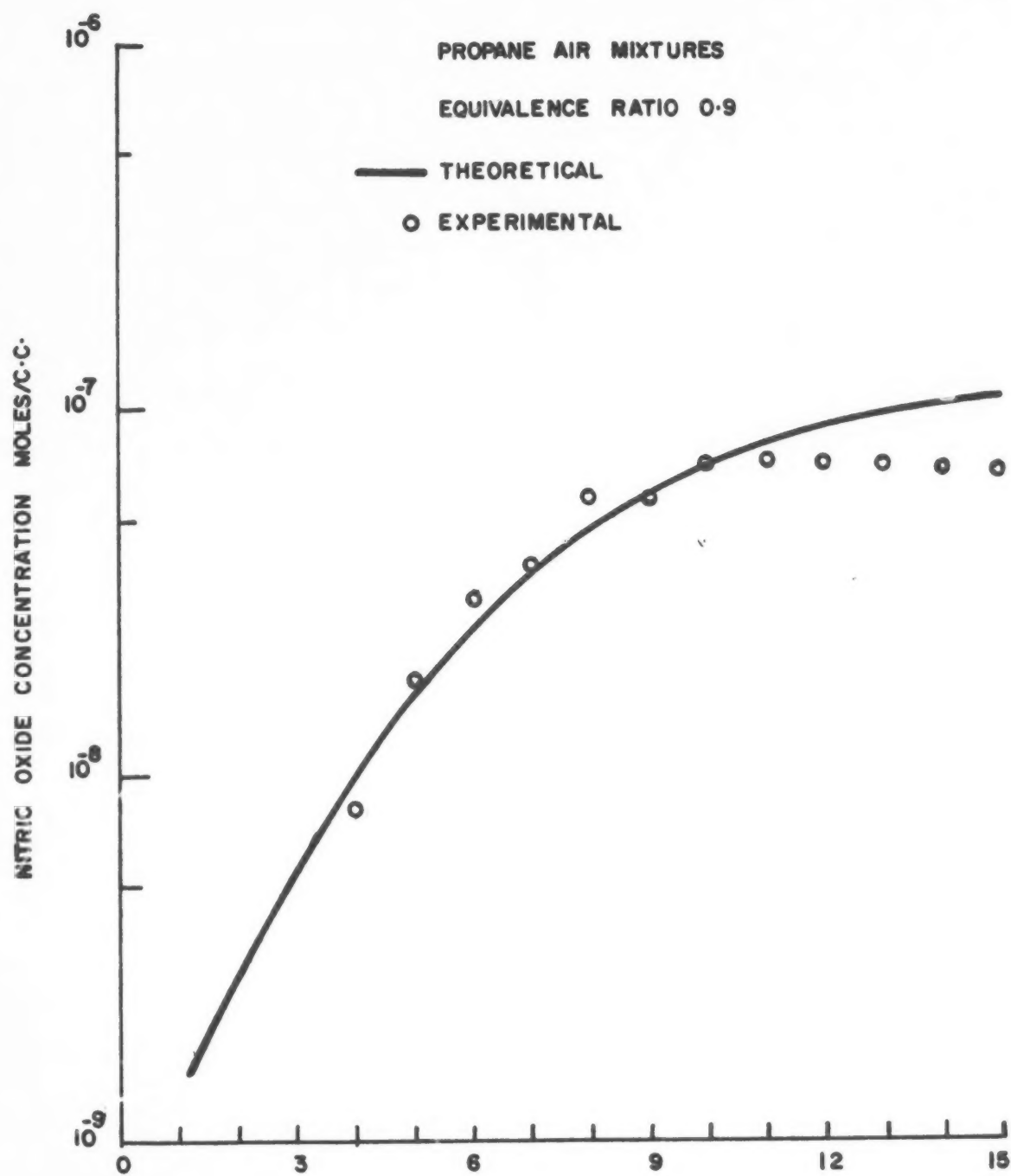
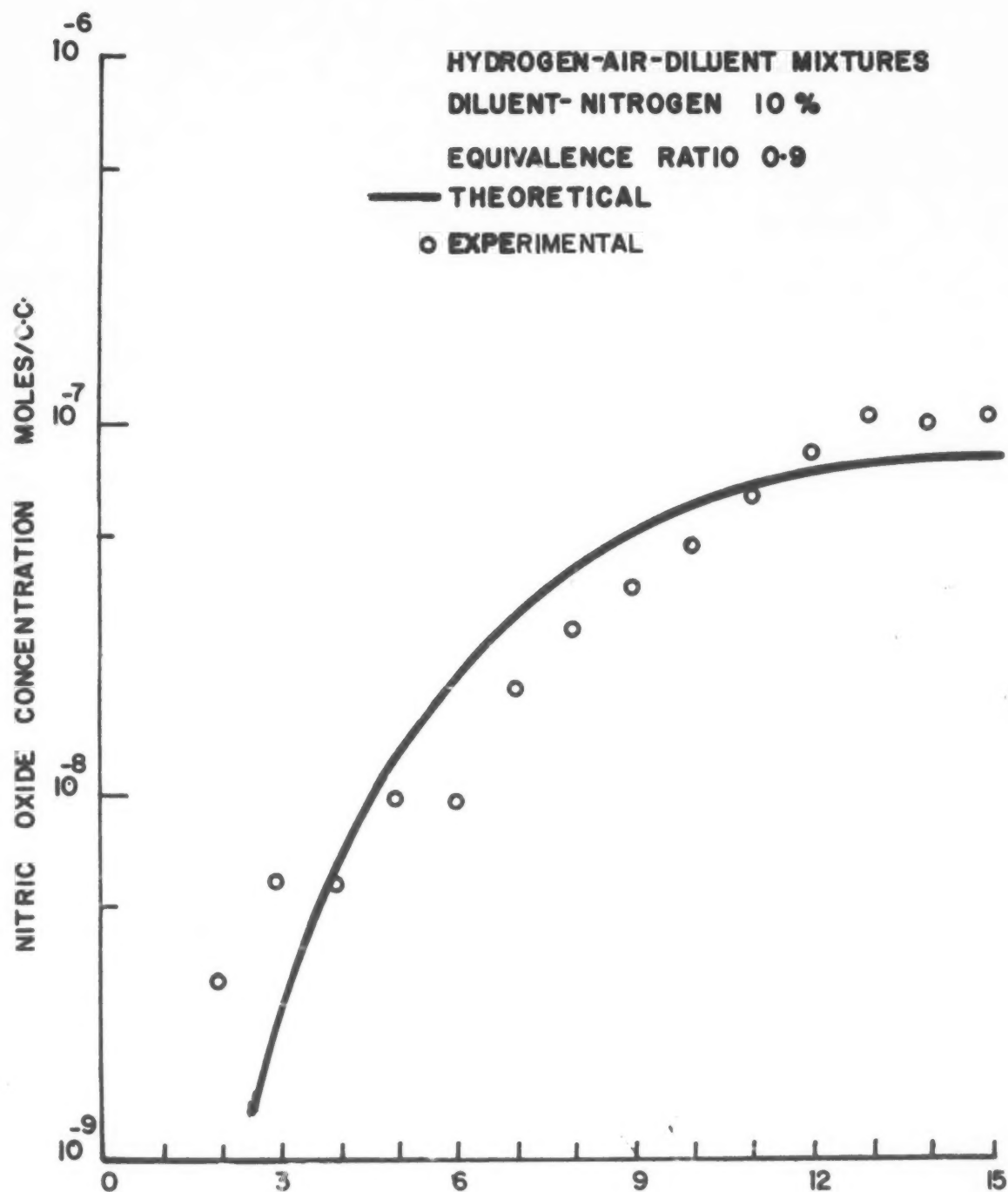


FIGURE 5.3



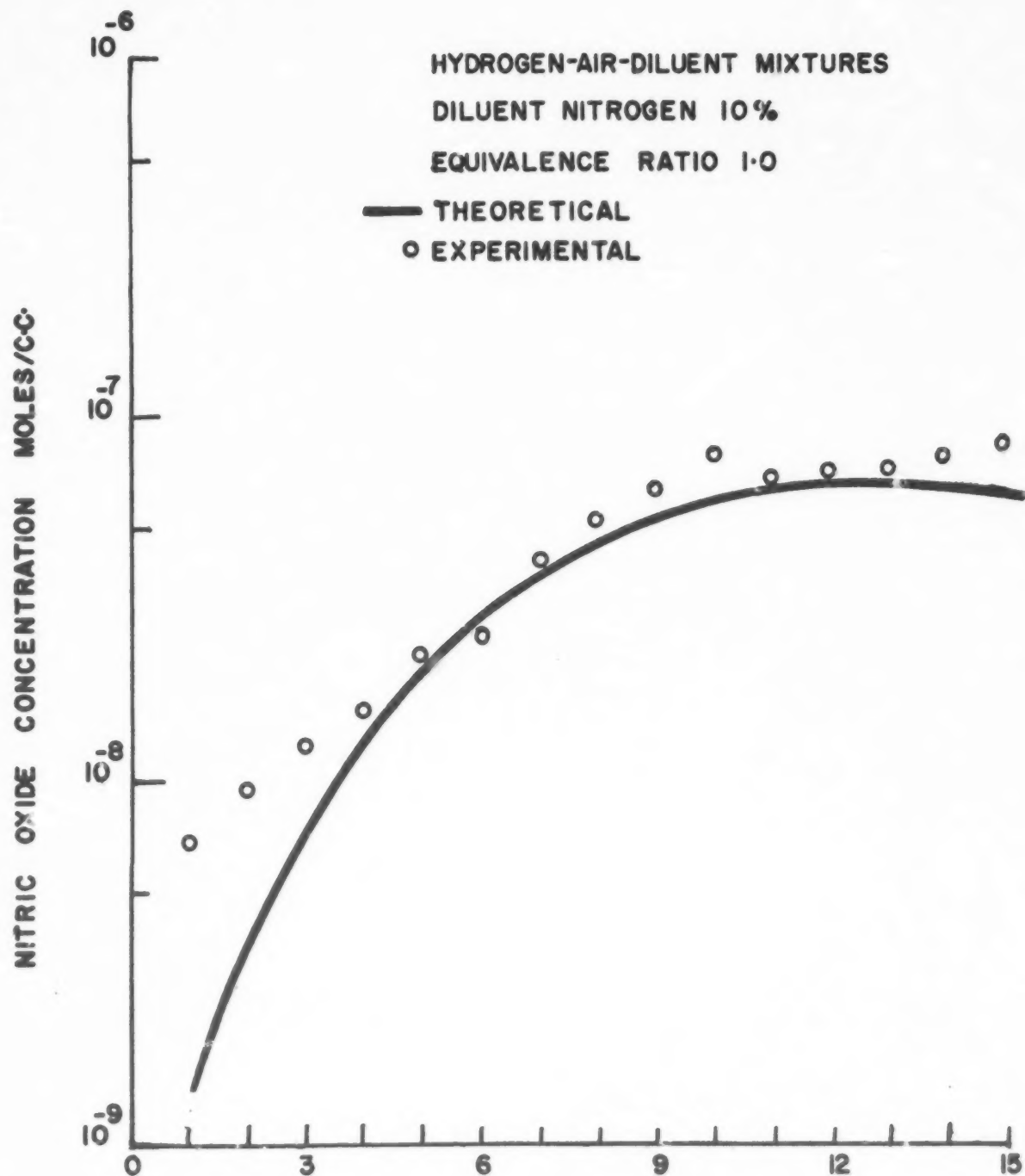
TIME (MILLISECONDS)
EXPERIMENTAL & THEORETICAL [NO]-TIME HISTORY

FIGURE 5-7



LABORATORY TIME MILLISECONDS
EXPERIMENTAL & THEORETICAL [NO]-TIME HISTORY

FIGURE 5.8



LABORATORY TIME - MILLISECONDS
EXPERIMENTAL & THEORETICAL [NO]-TIME HISTORY
FIGURE 5-6

A thorough review of the literature revealed a group of thirty elementary chemical reactions of importance in hydrogen-air oxidation kinetics. These reactions involve eleven chemical species including N, N₂, NO, N₂O, N₂O, O, O₂, H, OH, H₂, and H₂O. The elementary reactions employed are listed in Table V.I together with selected reaction rate constants and the references from which each of the rate constants was obtained.

Kinetic rate equations, one corresponding to each species, are obtained from this set of chemical reactions. The rate equations are of the general form

$$\frac{d[A_i]}{dt} = \sum_{j=1}^{30} v_{ij} K_j(T) \prod_{k=1}^{11} [A_k]^{v'_{kj}}$$

where $[A_i]$ = concentration of species A_i - $\frac{\text{moles}}{\text{cc}}$

v_{ij} = stoichiometric coefficient for species i in reaction j

(negative for reactants and positive for products).

v'_{kj} = stoichiometric coefficient for species k in reaction j

(positive for reactants and zero for products).

$K_j(T)$ = reaction rate constant for reaction j .

Eleven coupled non-linear, first order differential equations are thus obtained. These were integrated on a CDC 3600 digital computer employing a Runge Kutta procedure specially adopted to the problem. The initial condition employed in the integration procedure was a step

input in temperature bringing the temperature of reactants instantly to typical flame temperature levels. The stepwise integration procedure then yields the subsequent time-concentration history of each chemical species considered.

The results of these computations are shown in figures 5.10 thru 5.13. It is evident that $[O]$, $[O_2]$, $[N]$ and $[N_2]$ reach equilibrium concentrations in times of the order of magnitude of one tenth millisecond. Subsequent calculations and experimental results indicate that nitric oxide equilibration is relatively slow and equilibrium concentrations are reached in times of the order of magnitude of 20 milliseconds.

Hence it appears reasonable to assume that the species $[O]$, $[O_2]$, $[N]$, and $[N_2]$ reach and stay at equilibrium concentrations corresponding to the burnt gas temperatures and pressures. Further, the use of a step function as a temperature input may be questionable. But a consideration of the order of magnitude difference between 20 milliseconds and one tenth millisecond reinforces the above assumption for a temperature input that may not be a step function.

The second major assumption concerns the use of adiabatic flame temperatures for burnt gas temperatures. The arguments in favor of this assumption are less quantitative but no less conclusive.

It is argued that the flame is very fast burning, especially with hydrogen. Heat transfer, if any, is important for the gases near the walls, while the bulk of the gases in the optical path remain essentially adiabatic. Further it is pointed out that this assumption is extensively made in the literature, especially in view of the questionable nature of transient temperature measurement techniques presently available.

TABLE V.I
Elementary Chemical Reactions and Selected Rate Constants

<u>Reaction</u>	<u>Rate constant*</u>	<u>Reference</u>
1f. $\text{H}_2\text{O}+\text{M}\rightarrow\text{OH}+\text{H}+\text{M}$	$5.40 \times 10^{17} \exp(-123,600/\text{RT})$	(4), (46)
1b. $\text{H}+\text{OH}+\text{M}\rightarrow\text{H}_2\text{O}+\text{M}$	1.5×10^{16}	
2f. $\text{H}_2+\text{M}\rightarrow\text{H}+\text{H}+\text{M}$	$3.10 \times 10^{15} \exp(-110,000/\text{RT})$	(34), (30), (49)
2b. $\text{H}+\text{H}+\text{M}\rightarrow\text{H}_2+\text{M}$	$7.0 \times 10^{17} \sqrt{T}$	(44), (45)
3f. $\text{NO}+\text{M}\rightarrow\text{N}+\text{O}+\text{M}$	$7 \times 10^{10} \sqrt{T} \left(\frac{150,000}{\text{RT}} \right)^2 \exp(-150,000/\text{RT})$	(30), (52)
3b. $\text{N}+\text{O}+\text{M}\rightarrow\text{NO}+\text{M}$	0.9×10^{15}	
4f. $\text{N}_2+\text{M}\rightarrow\text{N}+\text{N}+\text{M}$	$4.2 \times 10^{12} \sqrt{T} \left(\frac{224,900}{\text{RT}} \right) \exp(-224,900/\text{RT})$	(34), (52), (2)
4b. $\text{N}+\text{N}+\text{M}\rightarrow\text{N}_2+\text{M}$	6.1×10^{14}	(18), (20)
5f. $\text{N}_2\text{O}+\text{M}\rightarrow\text{N}_2+\text{O}+\text{M}$	$1 \times 10^{15} \exp(-61,000/\text{RT})$	(23), (35)
5b. $\text{N}_2+\text{O}+\text{M}\rightarrow\text{N}_2\text{O}+\text{M}$	$1.82 \times 10^{13} \exp(-21,400/\text{RT})$	
6f. $\text{NO}_2+\text{M}\rightarrow\text{NO}+\text{O}+\text{M}$	$5.4 \times 10^{21} \left(\frac{1}{T} \right) \exp(-74,000/\text{RT})$	(9), (24)
6b. $\text{NO}+\text{O}+\text{M}\rightarrow\text{NO}_2+\text{M}$	2.0×10^{16}	(19), (42)

TABLE V.I CONTINUED

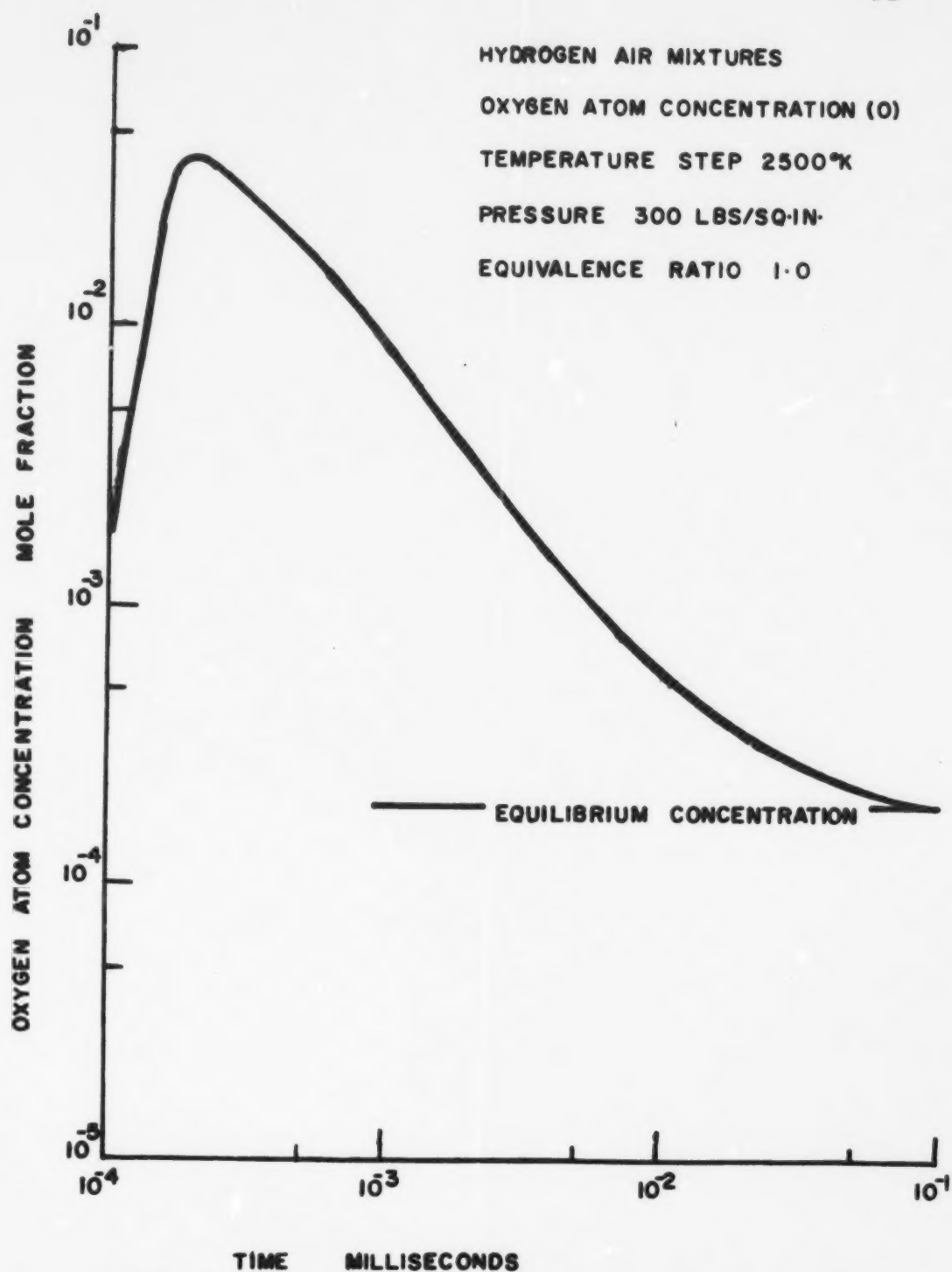
<u>Reaction</u>	<u>Rate constant*</u> $6 \times 10^{13} \left(\frac{118,000}{RT} \right) \exp(-118,000/RT)$ 1.0×10^{14}	<u>Reference</u> (34), (52), (17) (27), (31), (36)
7f. $O_2 + M \rightarrow O + M$		
7b. $O + O + M \rightarrow O_2 + M$		
8f. $OH + H \rightarrow H_2 + O$	$1.4 \times 10^{12} \exp(-6000/RT)$	(25)
8b. $H_2 + O \rightarrow OH + H$	$3.3 \times 10^{12} \exp(-8000/RT)$	
9f. $OH + O \rightarrow O_2 + H$	$5.5 \times 10^{13} \exp(-1000/RT)$	(25)
9b. $O_2 + H \rightarrow OH + O$	$7.2 \times 10^{14} \exp(-16,900/RT)$	
10f. $OH + H_2 \rightarrow H_2O + H$	$6.2 \times 10^{13} \exp(-6000/RT)$	(25)
10b. $H_2O + H \rightarrow OH + H_2$	$3.2 \times 10^{14} \exp(-21,100/RT)$	
11f. $OH + OH \rightarrow H_2O + O$	$7.7 \times 10^{12} \exp(-1000/RT)$	(25)
11b. $H_2O + O \rightarrow OH + OH$	$8.3 \times 10^{13} \exp(-18,100/RT)$	
12f. $NO + O \rightarrow O_2 + N$	$3.2 \times 10^9 \times T \times \exp(-39,100/RT)$	(52)
12b. $N + O_2 \rightarrow NO + O$	$13.3 \times 10^9 \times T \times \exp(-7080/RT)$	

TABLE V.I CONTINUED

<u>Reaction</u>	<u>Rate constant*</u>	<u>Reference</u>
13f. $\text{NO} + \text{N} + \text{N}_2 + \text{O}$	1.55×10^{13}	(52)
13b. $\text{N}_2 + \text{O} + \text{NO} + \text{N}$	$7 \times 10^{13} \exp(-75,500/\text{RT})$	
14f. $\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}$	$0.18 \times 10^{11} \sqrt{T} \exp(-47,000/\text{RT})$	(28)
14b. $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$	$0.58 \times 10^{11} \sqrt{T}$	
15f. $\text{NO} + \text{NO} + \text{N}_2 + \text{O} + \text{O}$	$2.6 \times 10^{12} \exp(-63,800/\text{RT})$	(26), (12)
15b. $\text{N}_2 + \text{O} + \text{O} + \text{NO} + \text{NO}$	$1.42 \times 10^{14} \exp(-28,000/\text{RT})$	

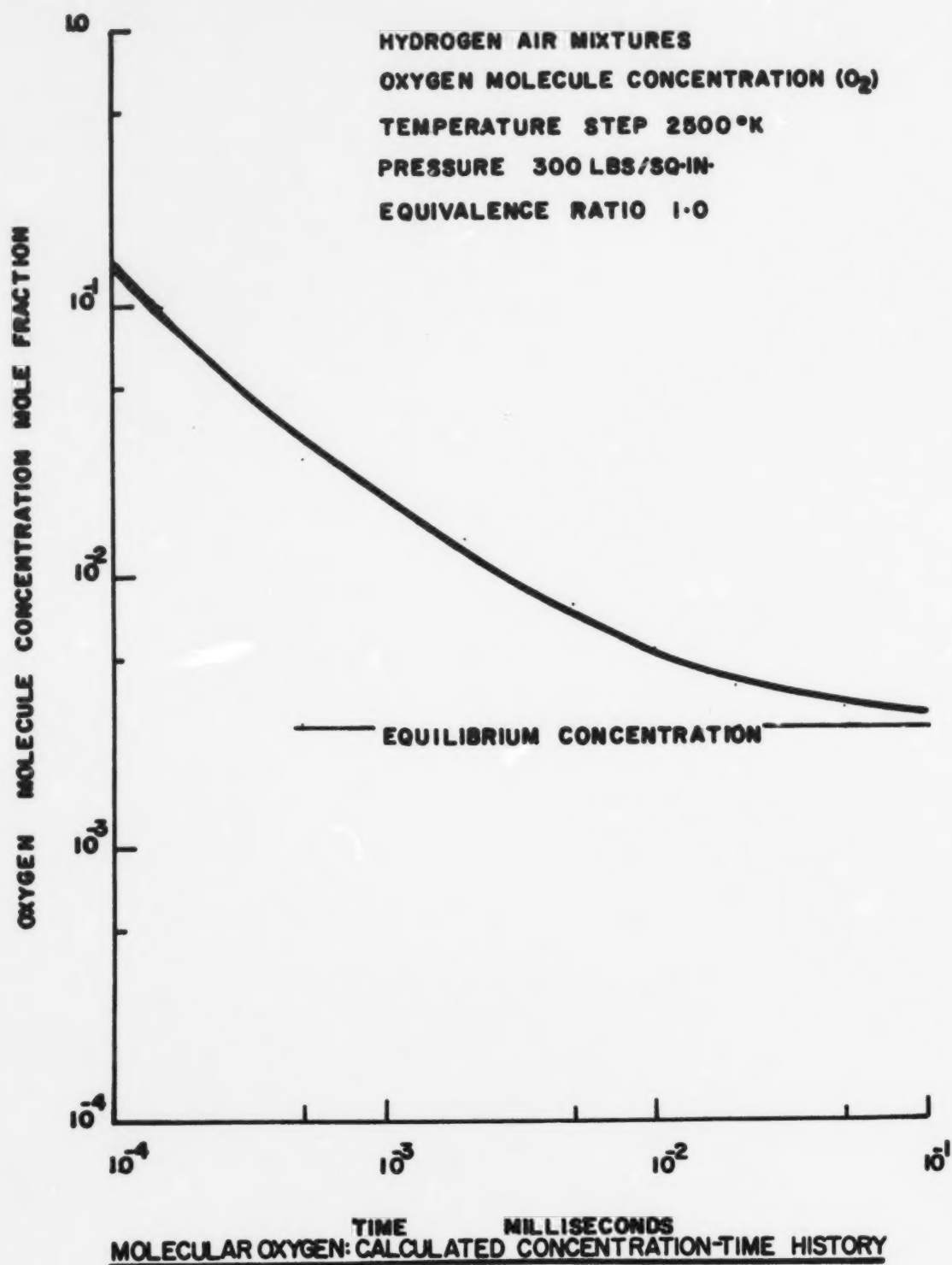
*Rate constant units: bimolecular reactions - $\text{cm}^3/\text{mole}\cdot\text{sec}$
 termolecular reactions - $\text{cm}^6/\text{mole}^2 \cdot \text{sec}$

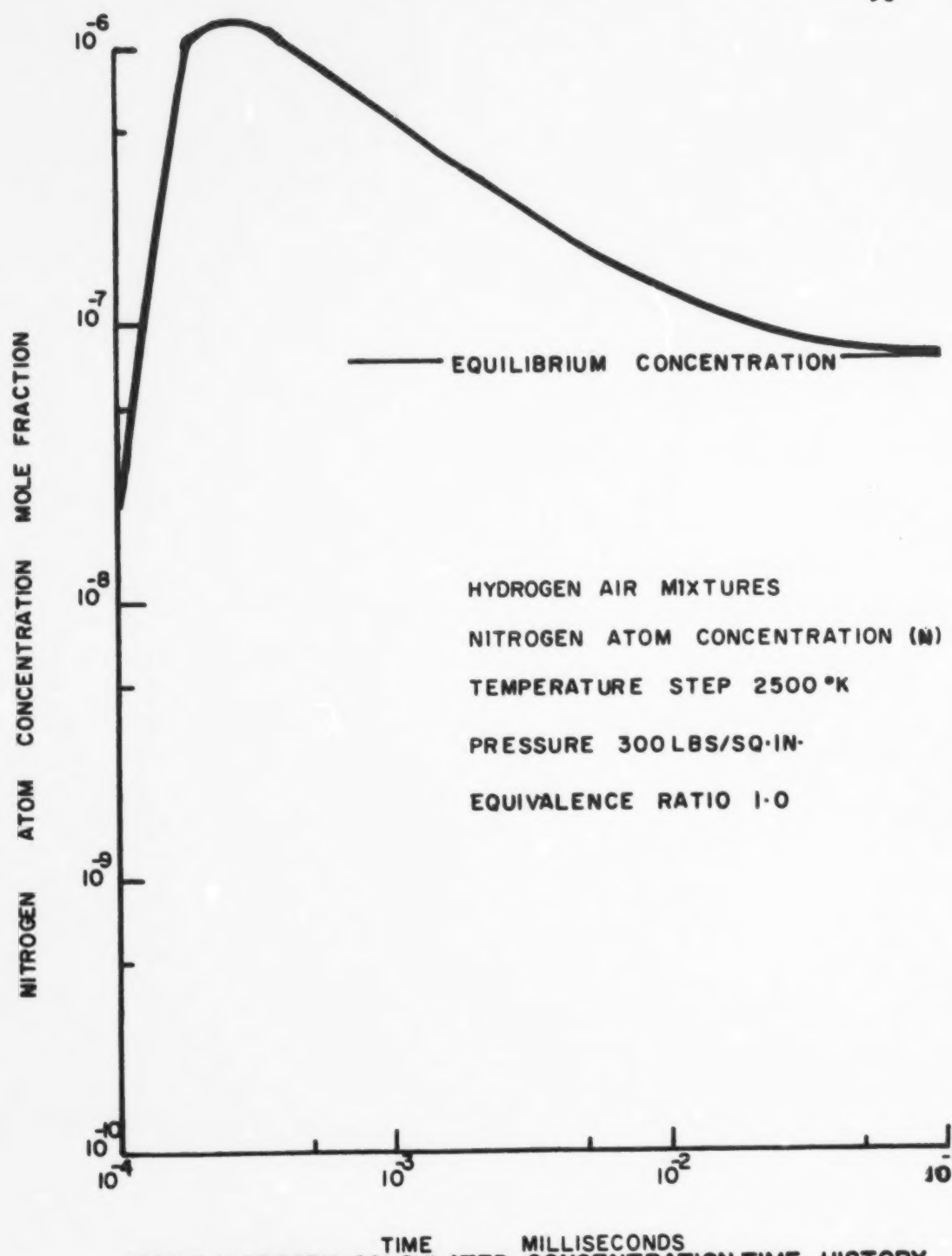
Third body, M, assumed to be N_2 .



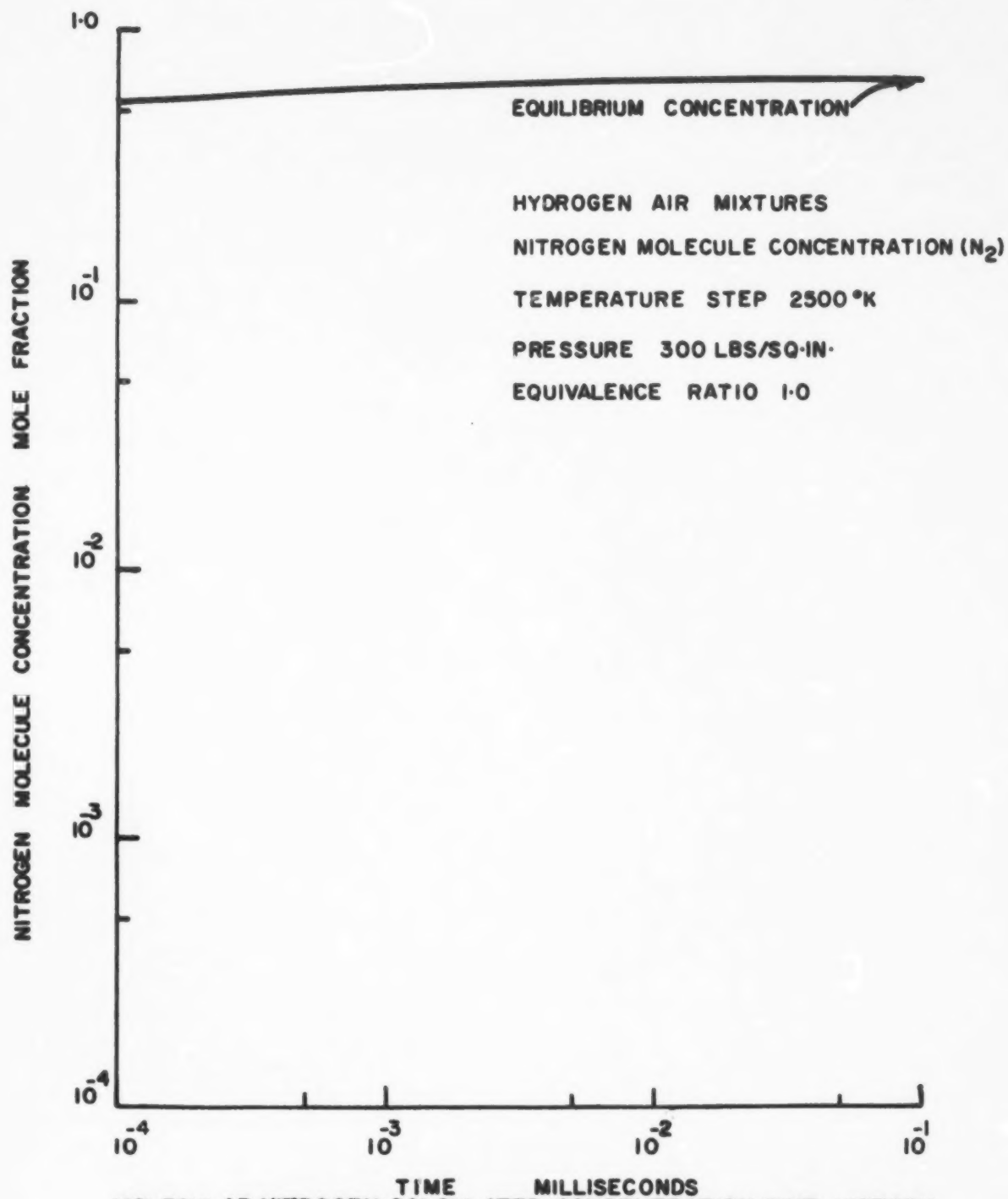
ATOMIC OXYGEN CALCULATED CONCENTRATION-TIME HISTORY

FIGURE 5-10

FIGURE 5-2



ATOMIC NITROGEN: CALCULATED CONCENTRATION-TIME HISTORY
FIGURE 5-12



MOLECULAR NITROGEN: CALCULATED CONCENTRATION TIME HISTORY

FIGURE 5-13

5.3 Discussion of Nitric Oxide Formation Mechanism:

Experimental results presented in article 3.6 lead to the conclusion that nitric oxide formation is a post flame phenomenon. Further, as discussed in article 5.2 the post flame relaxation of atoms and radicals to equilibrium concentrations is rapid compared to the rate of formation of nitric oxide, and the temperature of the burnt gases can be regarded as equal to the adiabatic flame temperature. Making use of these conclusions the set of formation reactions obtained from the literature and presented in article 4.1 was used to calculate nitric oxide concentration-time histories in post flame gases. The results of such calculations were compared with experimentally measured values. It was concluded that the formation of nitric oxide can be accurately predicted using a reaction mechanism consisting of the following two elementary reactions



The reaction mechanism proposed here was first suggested by N.N. Semenov and investigated in some detail by Zeldovich and coworkers (53,54). Their experiments, performed more than twenty years ago, lack any time or space resolution of nitric oxide formation, but the general conclusions arrived at in this work are in surprisingly close agreement with the conclusions of

Zeldovich et al.

5.3A Effect of Fuel

In the present work two fuels have been studied - hydrogen and propane. The same reaction mechanism has been used to calculate the formation of nitric oxide in the post flame gases. As is evident from figure 5.1 thru 5.9 the same reaction mechanism predicts the formation of nitric oxide for the two different fuels.

It might seem that further investigation of this aspect is warranted, yet, valuable conclusions can be drawn from the above results in conjunction with published literature.

It is argued that the formation of nitric oxide begins and continues in the post flame region, after the completion of combustion. It can then be concluded that for the present experiments the fuel had no effect on the formation mechanism of nitric oxide other than indirectly through stoichiometry (oxygen concentration in burnt gases) and flame temperatures.

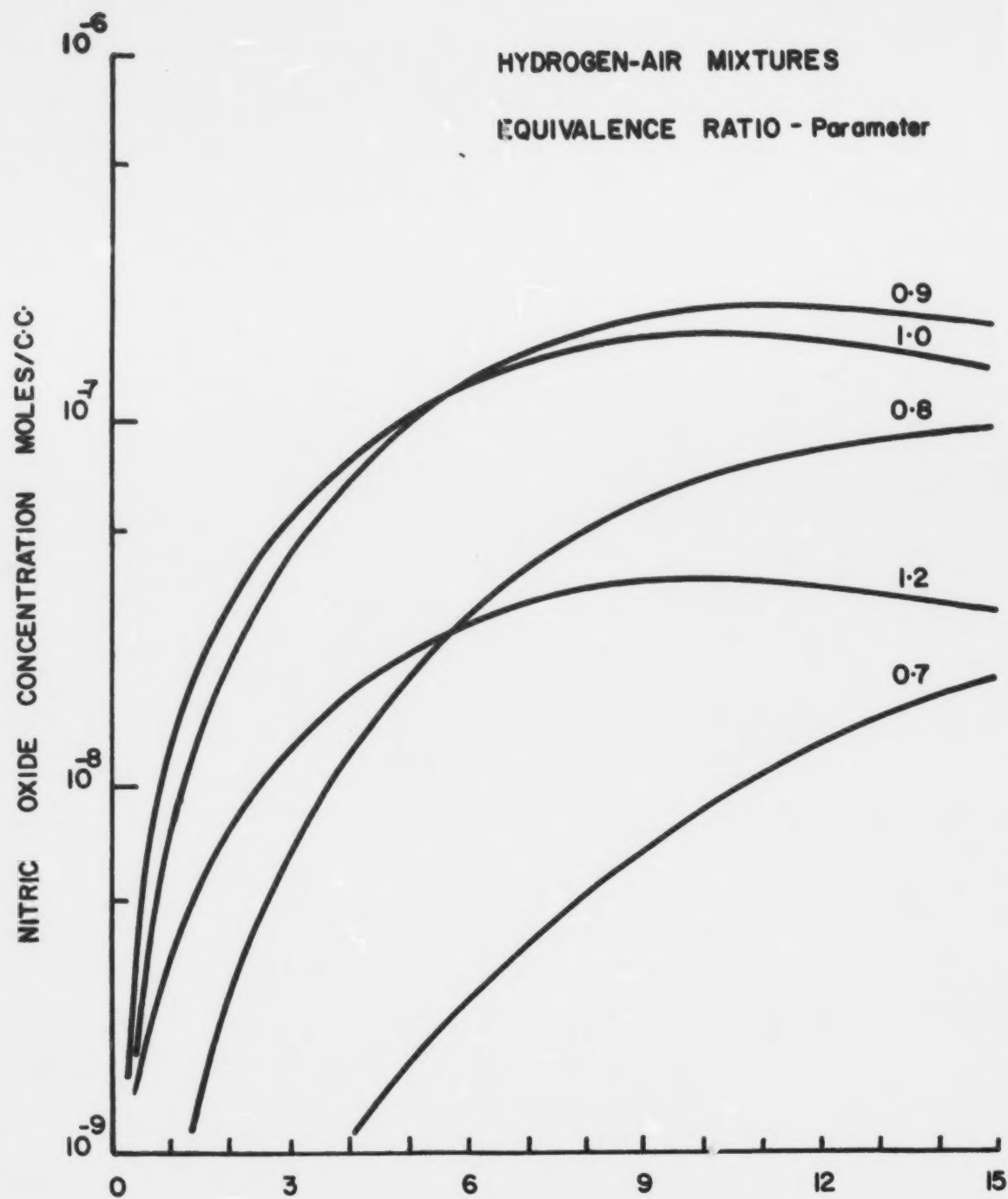
Similar conclusions are arrived at in the work of Zeldovich and coworkers, "The dependence of the amount of nitric oxide formed was studied as a function of mixture composition in the explosion of mixtures containing various combustibles; H_2 , CO, C_2H_4 , CH_4 with oxygen and nitrogen. In all mixtures, with the exception of the most dilute ones, at any given percentage of combustible,

the amount of NO is proportional to $\sqrt{N_2 \cdot O_2'}$ where O_2' is the concentration of oxygen in burnt products. The ratio $(NO/\sqrt{N_2 \cdot O_2'})$ increases uniformly with the combustible content of the mixture, i.e., with the increase in the combustion temperature; at approximately equal temperatures it is approximately equal for various fuels. Such an absence of any chemical specificity is an argument in favor of the thermal character of NO oxidation." (53)

Further in the same work the effect of initial temperature of explosive mixture on the amount of nitric oxide formed was investigated. It was concluded that --- "preheating is completely equivalent to the increase in the fuel content which is in agreement with the thermal point of view".

5.3B Effect of Equivalence Ratio

The effect of equivalence ratio (stoichiometry) on the rate of nitric oxide formation is indicated in figures 5.1 thru 5.5. The theoretical curves of these figures are reproduced for easy comparison in figure 5.14. It is evident that the approach to equilibrium, of nitric oxide is slower in lean mixtures than in stoichiometric or rich mixtures. It is argued that while the oxygen concentration in the burnt gases of lean mixtures is high, the temperature of these gases is low with a consequent decrease in reaction rate constants.



LABORATORY TIME MILLISECONDS
NITRIC OXIDE FORMATION RATE - EFFECT OF EQUIVALENCE RATIO

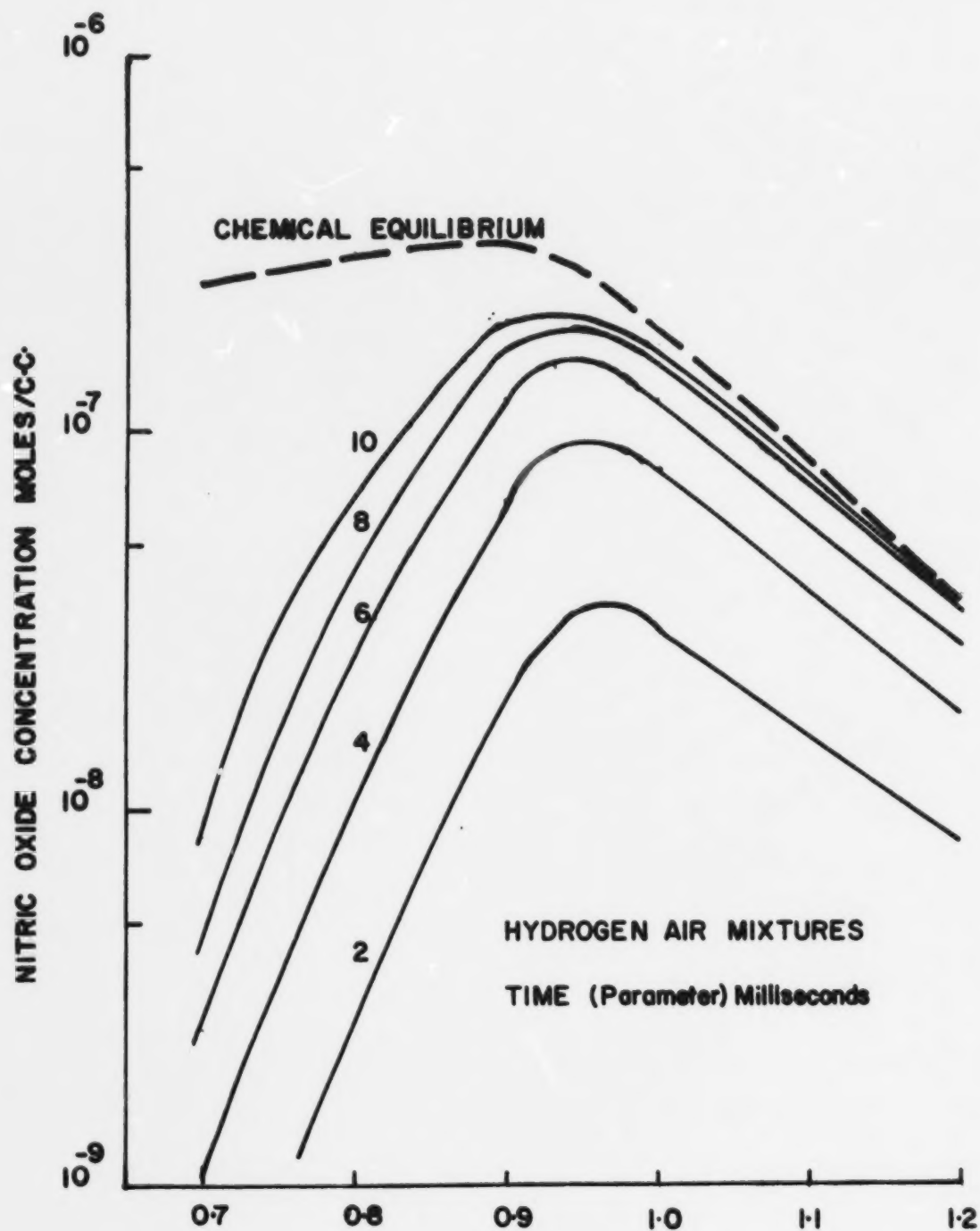
FIGURE 5-14

A number of parametric studies investigating the concentration of nitric oxide in engine exhaust gases at different equivalence ratios have been cited in article 1.1. It was pointed out that the qualitative conclusion drawn from these studies is that the formation of nitric oxide is dependent on the temperature and available oxygen concentration. As a result of the present investigation such qualitative conclusions are verified and given a quantitative shape through the use of the reaction mechanism, the reaction rate constants and species concentrations in burnt gases.

The approach of nitric oxide to equilibrium at different equivalence ratios is further illustrated in figure 5.15 where the concentration of nitric oxide is plotted against equivalence ratio at different instances of time. Also plotted is the equilibrium concentration at conditions corresponding to 15 milliseconds after inflammation at the optical path. It can be readily seen from figure 5.15 that the approach of nitric oxide to equilibrium concentrations is much faster in rich mixtures than in lean mixtures.

5.3C Effect of Reactant Dilution

The results of hydrogen-air diluent mixtures are presented in figures 5.8 and 5.9. The corresponding conditions without the diluent are presented in figures



FUEL-AIR EQUIVALENCE RATIO
NITRIC OXIDE APPROACH TO EQUILIBRIUM-EFFECT OF EQUIVALENCE RATIO

FIGURE 5-16

5.3 and 5.4. For easier comparison the theoretically calculated curves at equivalence ratios 0.9 and 1.0, at 0% and 10% dilutions are reproduced in figures 5.16 and 5.17.

It is evident from both calculations and measurements that a 10% dilution of charge results in better than 50% reduction in nitric oxide concentrations at the end of 15 milliseconds for both equivalence ratios.

5.4 Further Scope of This Work

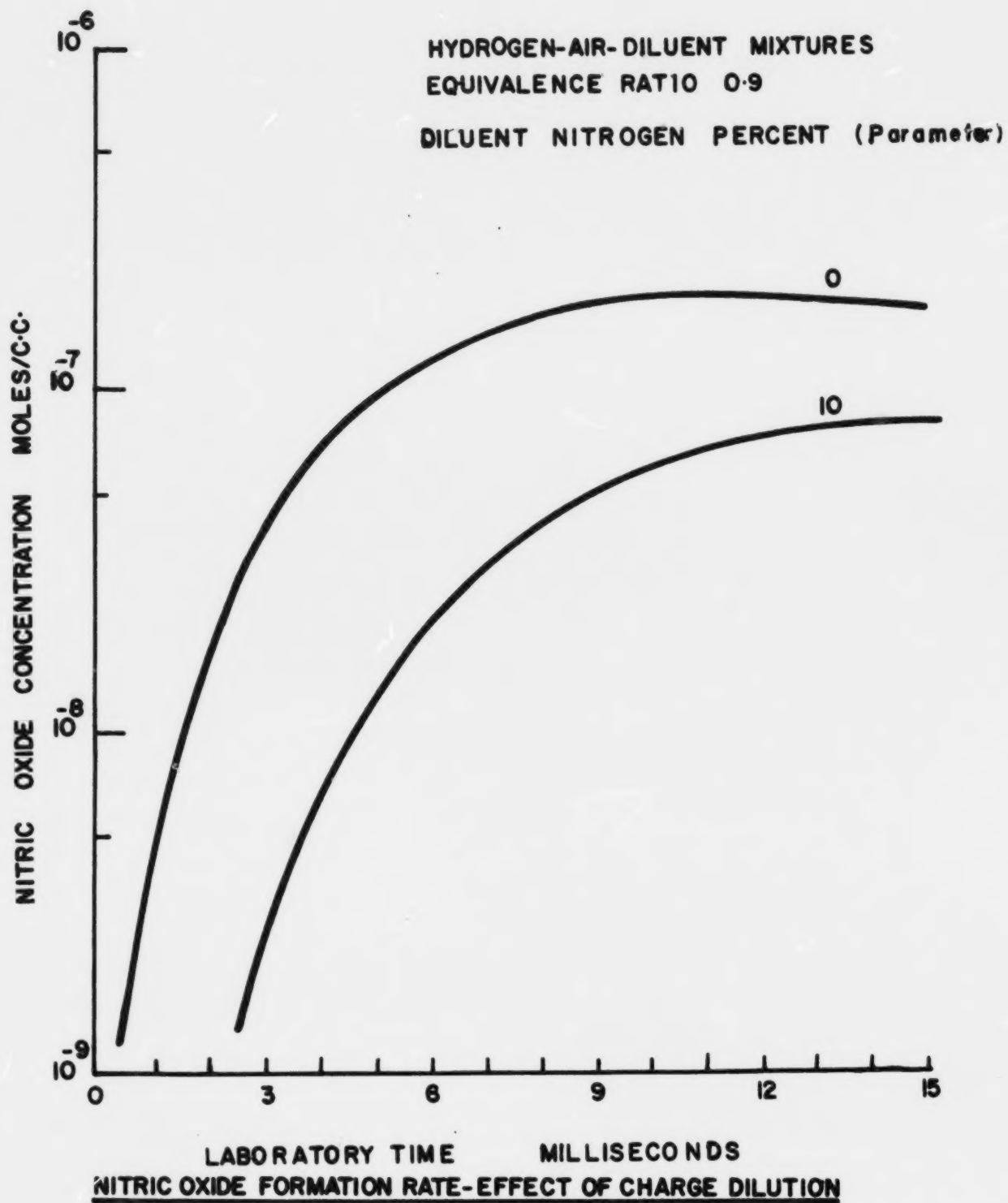
One substantial result of this work has been the development of a computer program which uses an experimentally measured pressure trace to predict concentration of nitric oxide in the optical path as a function of time.

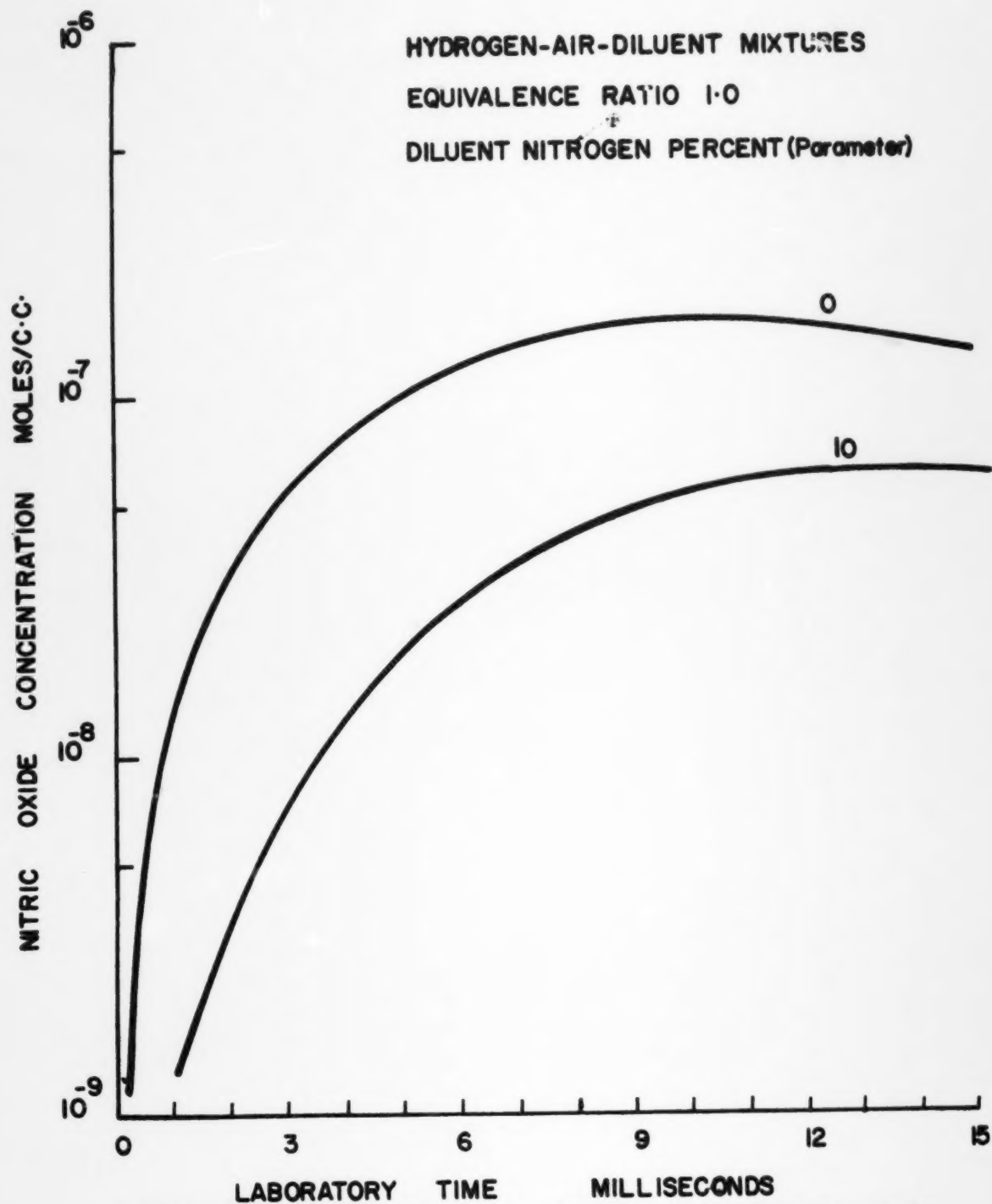
It is readily seen that the program can be altered with ease to give the total nitric oxide concentration in burnt gases taking into account the temperature gradients that exist therein. It is then a simple matter to feed in experimentally measured pressure traces from engines and obtain the average nitric oxide concentration versus time history.

Secondly, as was pointed out in article 5.3-A, there is need to investigate the effect of fuel variation more thoroughly.

5.5 Conclusions

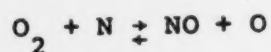
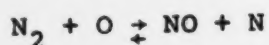
A) Nitric oxide formation was found to occur only

FIGURE 5-16

FIGURE 5-17

in the post flame gases, at a point in time after combustion reactions have ceased.

B) The formation of nitric oxide was found to be adequately predicted by a simple kinetic mechanism consisting of the following two reactions



A first order rate equation was obtained from the above mechanism. The solution of this equation gave the time rate of formation of nitric oxide.

C) The post flame relaxation of atoms and radicals to equilibrium concentrations was quantitatively estimated to be very fast compared to the formation of nitric oxide. It is concluded that in the rate equation for the formation of nitric oxide, equilibrium concentrations of atomic and molecular oxygen and nitrogen can be used.

D) The nitric oxide formation mechanism was found to be purely thermal in character and independent of the chemical nature of the fuel.

E) The rate of nitric oxide formation was found to be very sensitive to temperature and the concentration of available oxygen, increasing with an increase in either quantity.

F) The approach of nitric oxide to equilibrium at

different equivalence ratios was investigated. It was concluded that for near stoichiometric and rich mixtures the nitric oxide equilibration time is of the order of magnitude of combustion times generally available for earlier burning portions of charge in spark ignition engine processes. For lean mixtures nitric oxide equilibration is considerably slower due to a reduction in temperature. Consequently for lean mixtures nitric oxide does not reach equilibrium concentrations in times of the order of magnitude of combustion times generally available in engine cycles.

G) The effect of charge dilution on the rate of formation of nitric oxide was studied. It was found that the rate of formation is considerably slower in diluted mixtures than in undiluted mixtures of the same equivalence ratio. It was concluded that this effect is primarily due to a reduction in temperature of the burnt gases.

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APPENDIX ACalculation of Flame Position:

Article 4.4 describes the effect of flame propagation. This effect is felt through the convection of burnt gases past the optical path and is accounted for as a time correction in measured laboratory times. This correction is based on equation 4.4-4

$$\ln \frac{x_f}{x} = \frac{1}{\gamma} \ln \frac{p(t)}{p(\tau)} \quad 4.4-4$$

Where x_f the flame position at instant τ is calculated from the equation

$$x_f = \frac{\zeta \left(\frac{p}{p_i} \right)^{\frac{-1}{\gamma_u}} - 1}{\zeta \frac{T_i \left(\frac{p_i}{p} \right)^{\frac{\gamma_u - 1}{\gamma_u}}}{T_b \left(\frac{p}{p_i} \right)^{\frac{\gamma_u - 1}{\gamma_u}}} - 1} \quad A.1$$

Equation A.1 is derived from simple thermodynamic consideration as follows;

p	-	Pressure
T	-	Temperature
N	-	Number of moles
R	-	Universal Gas Constant
V	-	Volume
ζ	-	Number of moles of product per mole of Reactant

Subscripts

u	-	Unburnt gases
b	-	Burnt gases
i	-	Initial

The assumptions made are that the properties of products and reactants are uniform with the flame front acting as a pure discontinuity. Adiabatic conditions are assumed to prevail.

Conservation of mass;

$$N = N_u + N_b \quad \text{A.2}$$

$$V = V_u + V_b \quad \text{A.3}$$

Definition:

$$N_b = \zeta N_u$$

Ideal gas equation of state:

$$pV_b = N_b RT_b \quad \text{A.4}$$

$$pV_u = N_u RT_u \quad \text{A.5}$$

Isentropic comparison of unburnt gases:

$$T_u = T_i \left(\frac{p_i}{p_u} \right)^{\frac{\gamma_u - 1}{\gamma_u}}$$

Substitution of equation A.2 and A.3 into A.4 and use of the definition of ζ gives

$$p(V - V_b) = (N - \zeta \frac{pV_b}{RT_b}) RT_u$$

Simplification gives

$$pV - pV_b = NRT_u - \zeta pV_b \frac{T_u}{T_b}$$

or

$$v_b = \frac{NRT_u - pV}{\zeta p \frac{T_u}{T_b} - p}$$

Use of equation A.6 and further simplification gives

$$v_b = \frac{v \left(\frac{p}{p_i} \right)^{\frac{-1}{\gamma_u}} - 1}{\zeta \frac{T_i}{T_b} \left(\frac{p}{p_i} \right)^{\frac{\gamma_u - 1}{\gamma_u}} - 1}$$

Division by the constant area of cross section yields equation A.1

$$X_f = \frac{l \left(\frac{p}{p_i} \right)^{\frac{-1}{\gamma_u}} - 1}{\zeta \frac{T_i}{T_b} \left(\frac{p}{p_i} \right)^{\frac{\gamma_u - 1}{\gamma_u}} - 1} \quad \text{A.1}$$

Measured values of X_f , from ionization gap signals were used in conjunction with equation A.1 to calculate T_b the bulk temperature of burnt gases. Further, at the same instant τ using the pressure $p(\tau)$ the average bulk temperature of burnt gases was calculated using the method outlined in article 4.3. The two values of temperature agree very closely.

APPENDIX B 1
Data Reduction Program


```

C THIS PROGRAM COMPUTES NITRIC OXIDE CONCENTRATION BY ITERATION
C THE CONSTANT XK IS THE EXPOCIENT OF BEERS LAW.IT INCLUDES PATH LENGTH
C AND AFACTOR 10.0E-08
C THE TRIAL VALUE OF CONCENTRATION TO BE READ IN SHOULD NOT CONTAIN THIS
C FACTOR
  FIC1=A0+C+A1*C+C+A2*C*C+C+A3*C**4+XLOG
  FPIC1=A0+2.0*A1*C+3.0*A2*C*C+4.0*A3*C*C*C
  XK(C1)=A0+A1*C+A2*C*C+A3*C**4+C
  1 READ 100,K,TABS,PHI,PR,PHSC,TCF
100 FORMAT(7F10.0)
  IF(K-5) 7,2,2
  2 PRINT 300
300 FORMAT(1H1)
  PRINT 200,PHI,PR
200 FORMAT(1X,18MEQUIVALENCE RATIO=,F5.2,3X,17MINITIAL PRESSURE=,F5.1/
  1//)
  PRINT 400
400 FORMAT(1X,16H TIME      NO CONC,3X,34HABS COEFF    BROADENING    PRES
  1SURE)
  PRINT 600
600 FORMAT(1X,16HMSLCS    MOLES/CC,3X,32HCM**2/MOLE    PRESSURE    LBS/5
  10.1)
  6 READ 100,TIME,ABS1,ABS2,PB,C1,CF
  IF(C1-1000.0) 8,8,1
  8 CONTINUE
C CALCULATE EQUIVALENT BROADENING PRESSURE.
  PB=PHSC*PB+PR+14.7
  PRES=PB
  PB=SQRT(PB*(PR+14.7))-14.7
  FABS1=ABS1/TABS
  FABS2=ABS2*CF/TABS
  FTR1=1.0-FABS1
  FTR2=1.0-FABS2
  XLOG=LOGF(FTR1/FTR2)
  L=1
  IF(C1-2.0) 11,12,12
11 AU=8.85E-02-1.09E-05*PB+1.48E-10*PB*PB
  A1=8.52E-03-2.58E-05*PB+7.24E-08*PB*PB
  A2=-2.91E-03+2.30E-05*PB-4.55E-08*PB*PB
  A3=1.32E-03-4.56E-05*PB+6.15E-07*PB*PB-3.60E-09*PB*PB*PB+1.07E-11*
  1PB**4-1.11E-14*PB**5
  GO TO 3
12 IF(C1-8.0) 13,14,14
13 AU=1.01E-01-2.69E-04*PB+4.27E-07*PB*PB
  A1=1.27E-02-3.60E-04*PB+4.55E-06*PB*PB-1.94E-08*PB*PB*PB+2.67E-11*
  1PB**4
  A2=-5.18E-04-3.71E-06*PB+9.81E-09*PB*PB
  A3=8.85E-05-1.28E-06*PB-1.80E-08*PB*PB+4.05E-10*PB*PB*PB-2.00E-12*
  1PB**4+2.95E-15*PB**5
  3 C2=C1-F(C1)/F(C1)
  L=L+1
  IF(ABS(F(C2-C1))-1.0E-02) 5,4,4
  4 CONTINUE
  IF(L-22) 10,10,9
10 C1=C2
  IF(C1-2.0) 11,11,15

```

```

15 IF(C1-8.0) 13,13,14
5 XK1=XK(C2)*1.0E+08/(5.0*1.54)
GO TO 16
14 A=1.09E-01-1.26E-04*PB+9.64E-08*PB*PB
A1=C.0
A2=C.0
A3=C.0
C2=-XLOG/A0
XK1=XK(C2)*1.0E+08/(5.0*2.54)
16 C2=C2*1.0E-08*TCF
PRINT 500,TIME,C2,XK1,PB,PRES
500 FORMAT(F8.1,1X,E9.2,2X,E10.2,1X,E10.2,1X,F10.2)
GO TO 6
9 C2=C2*1.0E-08
C1=C1*1.0E-08
PRINT 700,TIME,C1,C2
700 FORMAT(50X,3F12.2)
GO TO 6
7 STOP
END

```

APPENDIX B 2

Nitric Oxide Formation Kinetics Program

[illegible]

000413	236.	TRF=TAU-TRFF
000416	237.	TRFF=1.0
000418	238.	00 10 21.1-50
000420	239.	TRFF=TRFF-0TRF
000421	240.	TRF=TRF-0TRF
000422	241.	TRF=20.01 21.2-28
000423	242.	3A CONTINUE
000424	243.	TRF=0TRF
000425	244.	TRF=0TRF
000426	245.	TRF=0TRF
000427	246.	TRF=0TRF
000428	247.	TRF=0TRF
000429	248.	TRF=0TRF
000430	249.	TRF=0TRF
000431	250.	TRF=0TRF
000432	251.	TRF=0TRF
000433	252.	TRF=0TRF
000434	253.	TRF=0TRF
000435	254.	TRF=0TRF
000436	255.	TRF=0TRF
000437	256.	TRF=0TRF
000438	257.	TRF=0TRF
000439	258.	TRF=0TRF
000440	259.	TRF=0TRF
000441	260.	TRF=0TRF
000442	261.	TRF=0TRF
000443	262.	TRF=0TRF
000444	263.	TRF=0TRF
000445	264.	TRF=0TRF
000446	265.	TRF=0TRF
000447	266.	TRF=0TRF
000448	267.	TRF=0TRF
000449	268.	TRF=0TRF
000450	269.	TRF=0TRF
000451	270.	TRF=0TRF
000452	271.	TRF=0TRF
000453	272.	TRF=0TRF
000454	273.	TRF=0TRF
000455	274.	TRF=0TRF
000456	275.	TRF=0TRF
000457	276.	TRF=0TRF
000458	277.	TRF=0TRF
000459	278.	TRF=0TRF
000460	279.	TRF=0TRF
000461	280.	TRF=0TRF
000462	281.	TRF=0TRF
000463	282.	TRF=0TRF
000464	283.	TRF=0TRF
000465	284.	TRF=0TRF
000466	285.	TRF=0TRF
000467	286.	TRF=0TRF
000468	287.	TRF=0TRF
000469	288.	TRF=0TRF
000470	289.	TRF=0TRF
000471	290.	TRF=0TRF
000472	291.	TRF=0TRF
000473	292.	TRF=0TRF
000474	293.	TRF=0TRF
000475	294.	TRF=0TRF
000476	295.	TRF=0TRF
000477	296.	TRF=0TRF
000478	297.	TRF=0TRF
000479	298.	TRF=0TRF
000480	299.	TRF=0TRF
000481	300.	TRF=0TRF
000482	301.	TRF=0TRF
000483	302.	TRF=0TRF
000484	303.	TRF=0TRF
000485	304.	TRF=0TRF
000486	305.	TRF=0TRF
000487	306.	TRF=0TRF
000488	307.	TRF=0TRF
000489	308.	TRF=0TRF
000490	309.	TRF=0TRF
000491	310.	TRF=0TRF
000492	311.	TRF=0TRF
000493	312.	TRF=0TRF
000494	313.	TRF=0TRF
000495	314.	TRF=0TRF
000496	315.	TRF=0TRF
000497	316.	TRF=0TRF
000498	317.	TRF=0TRF
000499	318.	TRF=0TRF
000500	319.	TRF=0TRF
000501	320.	TRF=0TRF
000502	321.	TRF=0TRF
000503	322.	TRF=0TRF
000504	323.	TRF=0TRF
000505	324.	TRF=0TRF
000506	325.	TRF=0TRF
000507	326.	TRF=0TRF
000508	327.	TRF=0TRF
000509	328.	TRF=0TRF
000510	329.	TRF=0TRF
000511	330.	TRF=0TRF
000512	331.	TRF=0TRF
000513	332.	TRF=0TRF
000514	333.	TRF=0TRF
000515	334.	TRF=0TRF
000516	335.	TRF=0TRF
000517	336.	TRF=0TRF
000518	337.	TRF=0TRF
000519	338.	TRF=0TRF
000520	339.	TRF=0TRF
000521	340.	TRF=0TRF
000522	341.	TRF=0TRF
000523	342.	TRF=0TRF
000524	343.	TRF=0TRF
000525	344.	TRF=0TRF
000526	345.	TRF=0TRF
000527	346.	TRF=0TRF
000528	347.	TRF=0TRF
000529	348.	TRF=0TRF

[illegible]

00010	169.	96 107-107-03
00011	170.	01722-0
00012	171.	00 16 12
00013	172.	99 107-107-03/102-001-01.0-001-03
00014	173.	07-01
00015	174.	00 16 11
00016	175.	100 024
00017	176.	07-000
00018	177.	000

END OF COMPILED: NO DISCREPANCIES.

APPENDIX CSample Data Reduction:

Experimental conditions;

Hydrogen - Air mixtures

Equivalence ratio 0.9

Initial Pressure 30 lbs./ sq. inch gauge.

Experimental procedure is described in article 3.2. A typical oscilloscope trace is shown in figure 3.3. For any given set of experimental conditions a thorough investigation of absorption at 2260 angstroms and at a range of wavelengths around 2260 angstroms is carried out. At each wavelength a large number of photographs similar to the one in figure 3.3 was taken. Reproducibility was found to be better than 5%. At least three photographs at each wavelength were taken.

A sample set of data for the experimental conditions given above is shown in table (1). Table (1) gives the absorption (cms - ordinate of the absorption trace in figure 3.3) at various instants of time at each recorded wavelength. Using this data plots similar to those in figure 3.4 and 3.5 are obtained. One such plot is shown in figure C 1 where absorption (cms) at 10 milliseconds after the arrival of the flame front in the optical path is plotted against wavelength. This gives the absorption due to Schumann-Runge bands of oxygen on which

the (0,0) gamma bands of nitric oxide are superimposed.

A correction factor CF is defined as follows;

$$CF = \frac{\text{Equivalent background absorption at nitric oxide Absorption frequency.}}{\text{Background absorption at a neighbouring frequency (2280 A.)}}$$

It is seen from figure C.1 that

$$CF = A/B$$

Plots similar to figure C.1 at different intervals of time after the arrival of the flame front in the optical path give the correction factor CF as a function of time. This is plotted in figure C.2. Ordinates of the pressure trace are also measured from the oscilloscope display photographs. This information is presented in table III. For any instant of time 't' table 3 gives the following information;

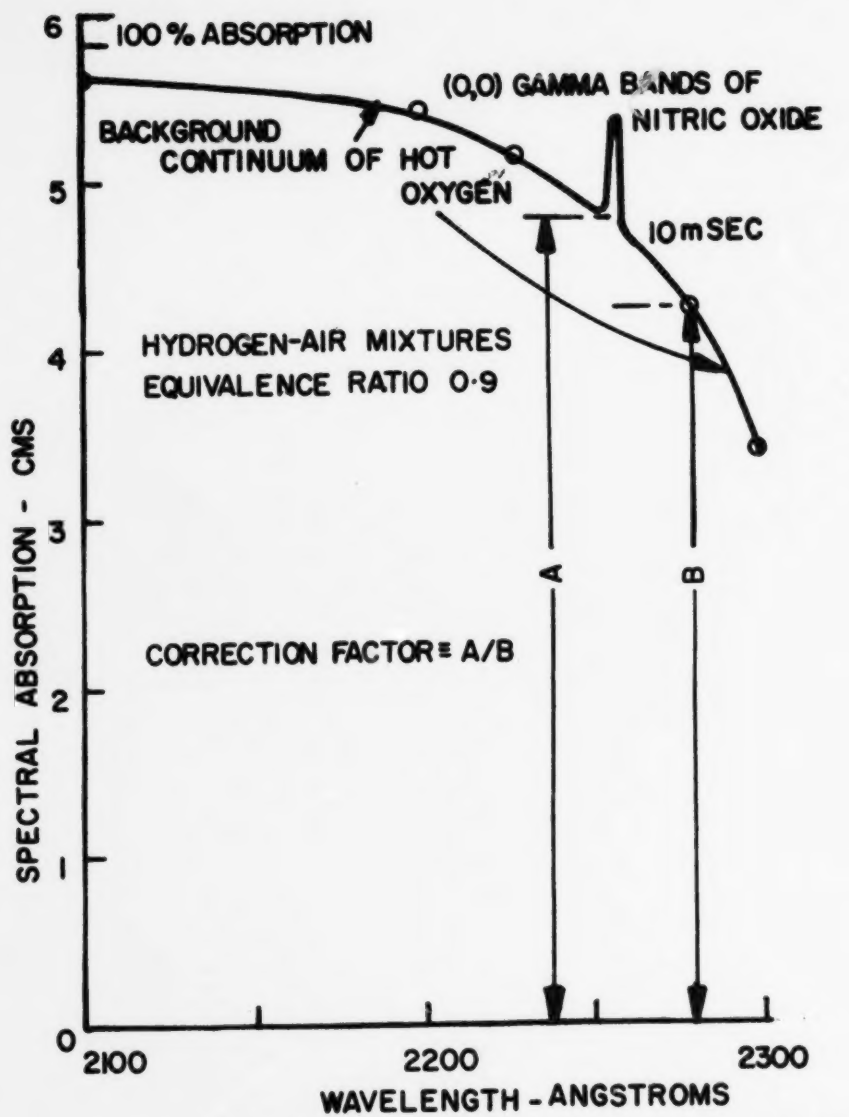
- (1) Absorption at nitric oxide absorption frequency.
- (2) Absorption at neighbouring frequency.
- (3) Ordinate of the pressure transducer output.
- (4) Trial value of nitric oxide concentration in moles/c.c. $\times 10^8$ for use in the computer reduction of data.
- (5) Correction factor as defined by equation C-1 and as obtained from the plot in figure C.2.

The computer program for data reduction is given in appendix B. Basically the procedure of data reduction

Table (1)

Sample Basic Data for Background and Nitric Oxide Absorption
 Hydrogen-Air Mixtures
 Initial Pressure - 30 psig
 Equivalence Ratio - 0.9
 Total Absorption Signal - 5.8 Cms.

Time Msec	Background Absorption (Cms)					Nitric Oxide Gamma Band Frequency
	Wavelength Angstroms					
	2100	2200	2230	2280	2300	
5	4.6	4.4	4.2	3.3	1.9	3.74
10	5.5	5.3	5.2	4.4	3.3	5.20
15	5.6	5.4	5.3	4.3	3.0	5.43
20	5.7	5.3	5.2	3.8	2.4	5.43
25	5.7	5.3	5.0	3.4	1.7	5.43
30	5.7	5.1	4.8	2.8	1.3	5.37



(0,0) GAMMA BAND OF NITRIC OXIDE SUPERIMPOSED
ON SCHUMANN RUNGE BANDS OF HOT OXYGEN

FIGURE C-1

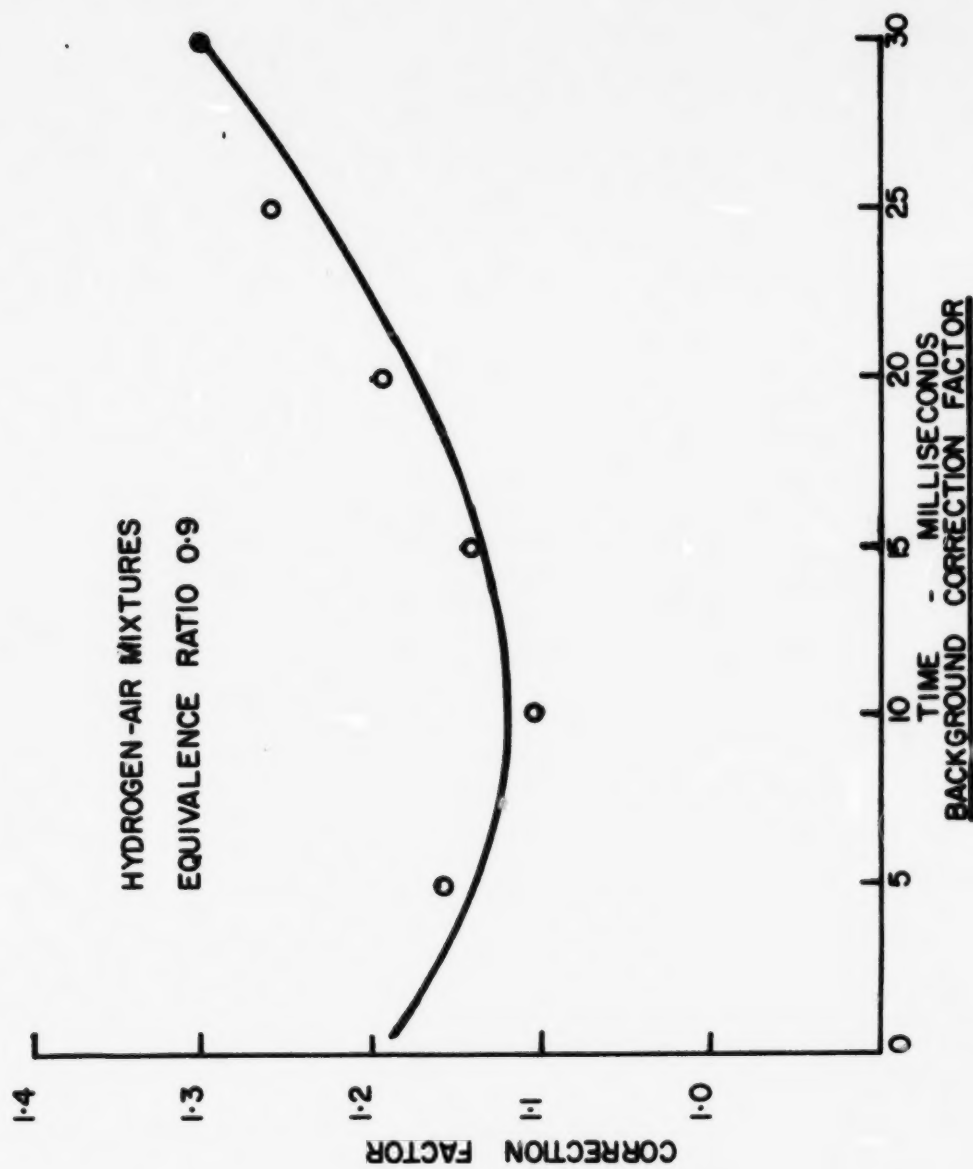


FIGURE C-2

consists in the solution of equation 3.5-3.

$$C = \frac{1}{K_{\lambda}(C,p)} \ln \left(\frac{1 - A_{\text{background}}}{1 - A_{\text{total}}} \right) \quad 3.5-5$$

The solution requires an iterative technique using a trial value of concentration. The trial values are given in column 4 of table III. A_{total} is the fractional spectral absorption due to nitric oxide and hot oxygen. This value is obtained from column 2 of table III. $A_{\text{background}}$ is calculated using the data of column 2 i.e. the spectral absorption at neighbouring frequency, multiplied by the correction factor given in column 5. The trial value of 'C' given in column 4 is then used to converge on the correct value of concentration.

The function $K_{\lambda}(C,p)$ is plotted in figures 3.1 and 3.2. The calibration data was fit with a polynomial to generate a function for use on the computer. This was done in the following manner. A function FUNC(C) was fit to each of the curves of constant pressure in figure 3.1

$$L K (C,p) \Big|_{\text{constant } p} = A_0 + A_1 C + A_2 C^2 + A_3 C^3$$

In order to improve accuracy of the fit it was found desirable to fit this function in three ranges of concentration. The values of the coefficients A_0 to A_3 were obtained in each concentration range and at each of the pressures shown. The

coefficients A_n were themselves fit with polynomial expressions as a function of pressure in each concentration range. Thus

$$A_0 = A_{00} + A_{01}p + A_{02}p^2 \text{ ----}$$

$$A_1 = A_{10} + A_{11}p + A_{12}p^2 \text{ ----}$$

$$A_2 = A_{20} + A_{21}p + A_{22}p^2 \text{ -----}$$

$$A_3 = A_{30} + A_{31}p + A_{32}p^2 \text{ -----}$$

The degree of each of these polynomials could be different in different concentration ranges in order to obtain optimum fits. The values of the coefficients A_{mn} for each concentration range are given in the Data Reduction Program listed in Appendix B.1. It should be noted the functions as fitted include the path length and a factor 10^{-8} moles/C.C. in the value of concentration 'C'.

TABLE I

Hydrogen-Air Mixtures
 Equivalence Ratio 0,7
 Initial Pressure 30psig

Total Absorption 5.8 Cms
 Pressure Scale 100 psi/Cm.

Time MSec	Absorption at Nitric Oxide (0,0) Gamma Band Cms.	Absorption at Neighboring Fre- quency 2280A Cms.	Pressure Signal Cms.	Trial Value of Concentration, 8 Moles/C.C. 10	Correction Factor
1.0	0.08	0.05	0.87	1.0	0.69
2.0	0.1	0.05	1.0	1.0	0.675
3.0	0.12	0.07	1.1	1.0	0.66
4.0	0.12	0.07	1.2	1.0	0.65
5.0	0.18	0.14	1.37	1.5	0.64
6.0	0.25	0.22	1.5	1.5	0.625
7.0	0.32	0.3	1.67	2.0	0.61
8.0	0.45	0.5	1.87	2.0	0.6
9.0	0.65	0.7	1.97	2.0	0.59
10.0	0.75	0.9	2.07	3.0	0.58
11.0	0.95	1.2	2.2	3.0	0.568
12.0	1.05	1.4	2.27	3.0	0.557
13.0	1.15	1.6	2.27	3.0	0.547
14.0	1.2	1.6	2.27	3.0	0.538
15.0	1.3	1.6	2.17	3.0	0.53
20.0	1.4	1.5	1.97	3.0	0.49
25.0	1.3	1.4	1.77	3.0	0.475
30.0	1.2	1.3	1.8	3.0	0.475
35.0	1.2	1.2	1.43	3.0	0.485

TABLE II

Hydrogen-Air Mixtures
Equivalence Ratio 0.8
Initial Pressure 30 psig

Total Absorption 5.8 Cws
Pressure Scale 100 psi/Cm.

Time mSec	Absorption at Nitric Oxide (O,O) Gamma Band Cms.	Absorption at Neigh- boring Fre- quency 2280 A Cms.	Pressure Signal Cms.	Trial Value of Concen- tration Moles/C.C. 10 ⁸	Correction Factor
1.0	0.3	0.1	1.03	1.0	1.36
2.0	0.6	0.38	1.23	1.5	1.33
3.0	1.07	0.7	1.47	2.0	1.31
4.0	1.6	1.08	1.83	3.0	1.29
5.0	2.3	1.45	2.1	3.0	1.27
6.0	2.84	1.95	2.43	3.0	1.26
7.0	3.5	2.35	2.6	4.0	1.25
8.0	3.95	2.8	2.6	5.0	1.24
9.0	4.27	3.05	2.5	6.0	1.23
10.0	4.56	3.3	2.4	6.0	1.225
11.0	4.76	3.35	2.4	6.0	1.20
12.0	4.93	3.38	2.3	6.0	1.20
13.0	5.08	3.38	2.2	6.0	1.2
14.0	5.13	3.35	2.13	6.0	1.20
15.0	5.2	3.35	2.03	6.0	1.20
20.0	5.26	3.0	1.73	6.0	1.238
25.0	5.26	2.5	1.53	6.0	1.285
30.0	5.24	2.15	1.33	6.0	1.36
35.0	5.18	1.75	1.15	6.0	1.47

TABLE III

Hydrogen-Air Mixtures
Equivalence Ratio 0.9
Initial Pressure 30 psig

Total Absorption 5.8 Cms.
Pressure Scale 100psi/Cm.

Time msec	Absorption at Nitric Oxide (O,O) Gamma Band Cms.	Absorption at Neighbouring Frequency 2280A. Cms.	Pressure Signal Cms.	Trial Value of Concentration Moles/C.C. 10^8	Correction Factor
1.0	0.685	0.25	1.2	2.0	1.25
2.0	1.5	0.75	1.57	2.0	1.22
3.0	2.33	1.5	1.99	2.0	1.2
4.0	3.13	2.1	2.4	3.0	1.17
5.0	3.74	2.7	2.7	3.0	1.16
6.0	4.28	3.1	2.8	4.0	1.16
7.0	4.6	3.5	2.72	4.0	1.15
8.0	4.87	3.8	2.6	5.0	1.14
9.0	5.07	3.9	2.5	6.0	1.138
10.0	5.2	3.95	2.42	6.0	1.13
11.0	5.3	4.0	2.27	6.0	1.13
12.0	5.3	4.05	2.17	6.0	1.13
13.0	5.4	4.0	2.07	6.0	1.13
14.0	5.43	4.0	2.0	6.0	1.131
15.0	5.43	3.8	1.9	6.0	1.132
20.0	5.43	3.6	1.5	6.0	1.16
25.0	5.43	3.4	1.2	6.0	1.21
30.0	5.37	3.2	1.03	6.0	1.28
35.0	5.27	2.8	0.87	6.0	1.38

TABLE IV

Hydrogen-Air Mixtures
Equivalence Ratio 1.0
Initial Pressure 30 psig

Total Absorption 5.8 Cms.
Pressure Scale 100 psi/Cm.

Time mSec	Absorption at Nitric Oxide (O ₂) Gamma Band Cms.	Absorption at Neighbouring Frequency 2280 A. Cms.	Pressure Signal Cms.	Trial Value of Concentration Moles/C.C. 10 ⁸	Correction Factor
1.0	0.77	0.45	1.6	2.0	1.142
2.0	1.87	1.15	2.05	2.0	1.14
3.0	2.87	1.9	2.65	4.0	1.132
4.0	3.7	2.75	2.95	4.0	1.13
5.0	4.23	3.35	2.8	4.0	1.125
6.0	4.57	3.7	2.7	6.0	1.122
7.0	4.83	3.95	2.57	8.0	1.12
8.0	5.0	4.1	2.47	8.0	1.12
9.0	5.1	4.17	2.3	8.0	1.12
10.0	5.2	4.23	2.2	8.0	1.12
11.0	5.2	4.2	2.1	8.0	1.12
12.0	5.27	4.15	2.0	8.0	1.12
13.0	5.27	4.08	1.9	7.0	1.122
14.0	5.3	3.95	1.35	7.0	1.125
15.0	5.3	3.85	1.8	8.0	1.13
20.0	5.23	3.5	1.45	6.0	1.17
25.0	5.1	2.85	1.15	6.0	1.23
30.0	4.97	2.2	1.0	6.0	1.33
35.0	4.73	1.4	0.85	6.0	1.47

TABLE V

Hydrogen-Air Mixtures
Equivalence Ratio 1.2
Initial Pressure

Total Absorption
Pressure Scale 100 psi/Cm.

Time mSec	Absorption at Nitric Oxide (O ₂ O) Gamma Band Cms.	Absorption at Neighbour- ing Frequency 2280 A. Cms.	Pressure Signal Cms.	Trial Value of Concen- tration Moles/C.C. 10 ⁸	Correction Factor
1.0	1.9	1.4	1.6	2.0	1.2
2.0	3.7	3.0	2.3	2.0	1.15
3.0	4.70	4.1	3.0	2.0	1.1
4.0	5.3	4.7	3.0	3.0	1.09
5.0	5.55	5.0	2.9	3.9	1.09
6.0	5.65	5.0	2.8	3.0	1.08
7.0	5.65	5.0	2.7	3.0	1.08
8.0	5.65	4.95	2.55	3.0	1.10
9.0	5.60	4.90	2.40	3.0	1.10
10.0	5.60	4.87	2.30	5.0	1.10
11.0	5.60	4.80	2.16	5.0	1.11
12.0	5.5	4.6	2.05	5.0	1.12
13.0	5.4	4.5	1.92	5.0	1.13
14.0	5.3	4.4	1.86	5.0	1.14
15.0	5.2	4.3	1.78	5.0	1.15
16.0	5.1	4.1	1.7	5.0	1.16
17.0	5.1	4.0	1.62	5.0	1.17
19.0	5.0	3.92	1.56	5.0	1.18

TABLE VI

Propane-Air Mixtures
 Equivalence Ratio 0.8
 Initial Pressure 30 psig

Total Absorption 6.3 Cms.
 Pressure Scale 40 psi/Cm.

Time mSec	Absorption at Nitric Oxide (O,O) Gamma Band Cms.	Absorption at Neigh- bourhood Frequency 2280 A. Cms.	Pressure Signal Cms.	Trial Value of Concen- tration Moles/C.C. ⁸ ₁₀	Correction Factor
5.0	0.1	0.0	1.84	2.0	2.8
6.0	0.2	0.0	1.89	2.0	2.5
7.0	0.4	0.0	1.94	2.0	2.2
8.0	0.5	0.05	1.97	2.0	2.0
9.0	0.97	0.12	2.01	3.0	1.75
10.0	1.43	0.33	2.06	3.0	1.5
11.0	2.07	0.70	2.1	3.0	1.5
12.0	2.77	1.27	2.15	3.15	1.20
13.0	3.23	1.70	2.20	6.0	1.15
14.0	3.60	2.07	2.25	6.0	1.10
15.0	3.93	2.57	2.30	6.0	1.08
16.0	4.3	2.97	2.35	6.0	1.08
17.0	4.60	3.33	2.40	6.00	1.07
18.0	4.83	3.53	2.56	6.0	1.07
19.0	4.97	3.67	2.52	6.00	1.06
20.0	5.07	3.83	2.58	6.0	1.06

TABLE VII

Propane-Air Mixture
Equivalence Ratio 0.9
Initial Pressure 30 psig

Total Absorption 6.3 Cms.
Pressure Scale 40 psi/Cm.

Time mSec	Absorption at Nitric Oxide (O,O) Gamma Band Cms.	Absorption at Neighbour- ing Fre- quency 2280 Å. Cms.	Pressure Signal Cms.	Trial Value of Concen- tration Moles/C.C. 10^8	Correction Factor
3.0	0.02	0.0	1.90	2.0	1.6
4.0	0.47	0.0	1.95	2.0	1.5
5.0	1.05	0.0	2.00	2.0	1.40
6.0	1.62	0.05	2.06	3.0	1.3
7.0	2.22	0.4	2.13	3.0	1.22
8.0	3.38	1.25	2.19	3.0	1.19
9.0	4.16	2.10	2.25	3.0	1.10
10.0	4.73	2.70	2.31	4.0	1.10
11.0	5.10	3.40	2.38	4.0	1.08
12.0	5.60	4.40	2.45	4.0	1.08
13.0	5.70	4.85	2.55	4.0	1.07
14.0	5.83	4.90	2.63	5.0	1.07
15.0	5.90	5.05	2.72	5.0	1.07
16.0	6.01	5.15	2.82	5.0	1.06
17.0	6.1	5.30	2.91	6.0	1.06
18.0	6.17	4.40	3.01	6.0	1.06
19.0	6.19	5.60	3.10	6.0	1.06
20.0	6.25	5.75	3.20	6.0	1.05

TABLE VIII

Hydrogen-Air-Diluent

Charge Dilution 10%

Equivalence 0.9

Total Initial Pressure 30 psig

Total Absorption 6.3 Cms.

Pressure Scale 100 psi/Cm.

Time mSec.	Absorption at Nitric Oxide (O ₂) Gamma Band Cms.	Absorption at Neigh- bouring Frequency 2280 Å. Cms.	Pressure Signal Cms.	Trial Value of Concen- tration Moles/C.C. ⁸ 10	Correction Factor
1.00	0.50	0.30	1.10	2.00	1.55
2.00	1.15	0.70	1.40	2.00	1.50
3.00	1.90	1.20	1.60	2.00	1.45
4.00	2.50	1.70	1.80	2.00	1.39
5.00	3.15	2.20	2.13	2.00	1.34
6.00	3.55	2.60	2.43	4.00	1.30
7.00	4.10	3.00	2.70	4.00	1.27
8.00	4.38	3.30	2.76	6.00	1.21
9.00	4.50	3.45	2.80	6.00	1.19
10.0	4.72	3.55	2.70	6.00	1.18
11.0	4.82	3.50	2.66	6.00	1.18
12.0	4.95	3.45	2.60	6.00	1.18
13.0	5.05	3.40	2.56	6.00	1.18
14.0	5.10	3.35	2.46	6.00	1.18
15.0	5.12	3.30	2.30	6.00	1.19
16.0	5.20	3.25	2.20	6.00	1.20
17.0	5.30	3.20	2.10	6.00	1.21
18.0	5.40	3.15	2.00	6.00	1.22
19.0	5.40	3.10	2.00	6.00	1.24

TABLE IX

Hydrogen-Air-Diluent Mixtures
 Charge Dilution 10%
 Equivalence Ratio 1.0
 Total Initial Pressure 30 psig

Total Absorption 6.3 Cms.
 Pressure Scale 40 psi/Cm.

Time mSec	Absorption at Nitric Oxide (O,O) Gamma Band Cms.	Absorption at Neigh- bouring Frequency 2280 A. Cms.	Pressure Signal Cms.	Trial Value of Concen- tration Moles/C.C. 10^8	Correction Factor
1.00	0.80	0.40	1.25	2.00	1.39
2.00	1.76	1.10	1.65	2.00	1.34
3.00	2.65	1.80	2.00	2.00	1.30
4.00	3.43	2.50	2.40	2.00	1.25
5.00	4.13	3.10	2.75	4.00	1.22
6.00	4.60	3.60	3.00	4.00	1.19
7.00	5.00	3.95	2.90	4.00	1.17
8.00	5.10	4.00	2.80	4.00	1.16
9.00	5.20	4.05	2.70	4.00	1.15
10.0	5.26	4.05	2.60	6.00	1.14
11.0	5.15	4.00	2.50	6.00	1.14
12.0	5.12	3.95	2.40	6.00	1.14
13.0	5.10	3.90	2.30	6.00	1.14
14.0	5.10	3.82	2.20	6.00	1.15
15.0	5.10	3.75	2.10	6.00	1.16
16.0	5.10	3.70	2.00	6.00	1.17
17.0	5.06	3.60	2.00	6.00	1.18
18.0	4.96	3.50	1.90	6.00	1.19
19.0	4.88	3.40	1.90	6.00	1.20

APPENDIX D

Ionisation Gap Circuit:

The circuit for use with a single ionisation gap is shown in figure D.1A. The capacitor, C, 100 pF is charged to 300 Volts through the charging resistor, R_C , 22M. The arrival of the flame front at the gap is detected by a discharge of the condensor across it. This gives a negative voltage pulse across R_1 , the load resistor. The firing of the gap is equivalent to the closing of the switch in the circuit shown in figure D.1B. In this figure R_g is the equivalent gap resistance when it fires.

The charging resistor R_C , needs to be high so that the condensor remains effectively discharged during the time the gap is exposed to post flame ionisation. The signal rise time is governed by the rate of discharge of C through the gap impedance. A small value of C must therefore be used in order to obtain fast response.

In order to use this method on a series of detectors the circuit shown in figure D.1C is employed. The diodes prevent the shorting of the signals by the other detectors.

Deuterium Lamp Power Supply:

The dueterium lamp used, Sylvania DE 350, requires a starting voltage of 100 Volts DC and a running voltage of 40 Volts DC at 0.8 Amps. Further the filament of the lamp requires 15 Amps at 4 Volts AC starting and is to be cut out once the lamp has fired. This is accomplished by means of

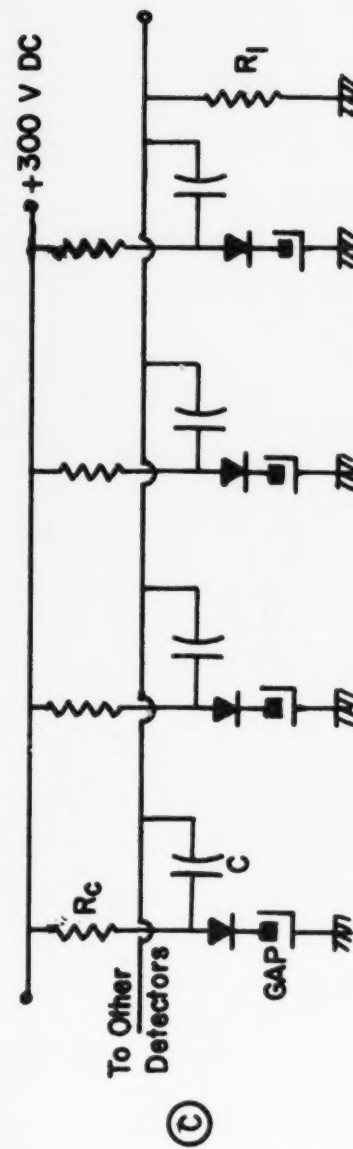
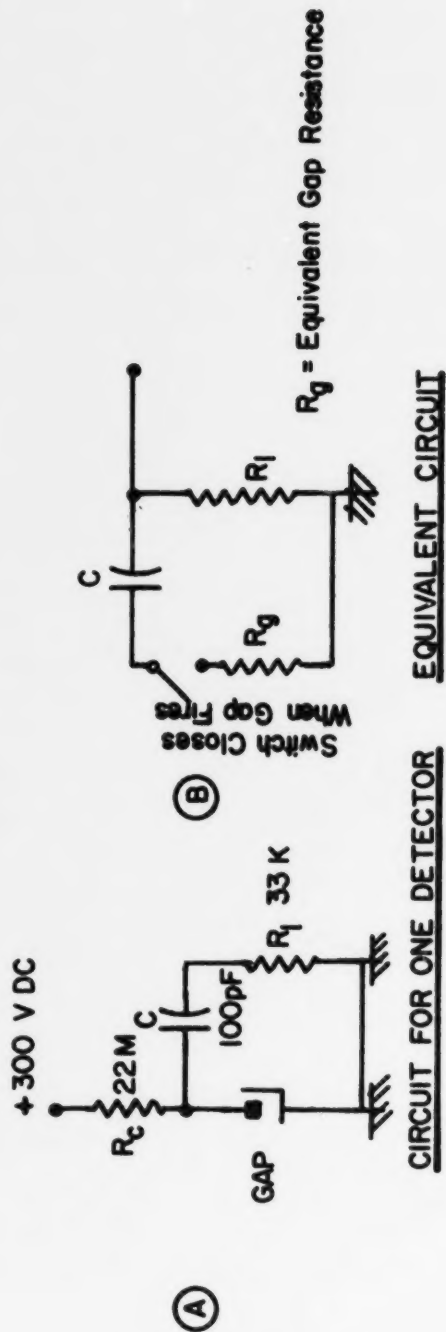
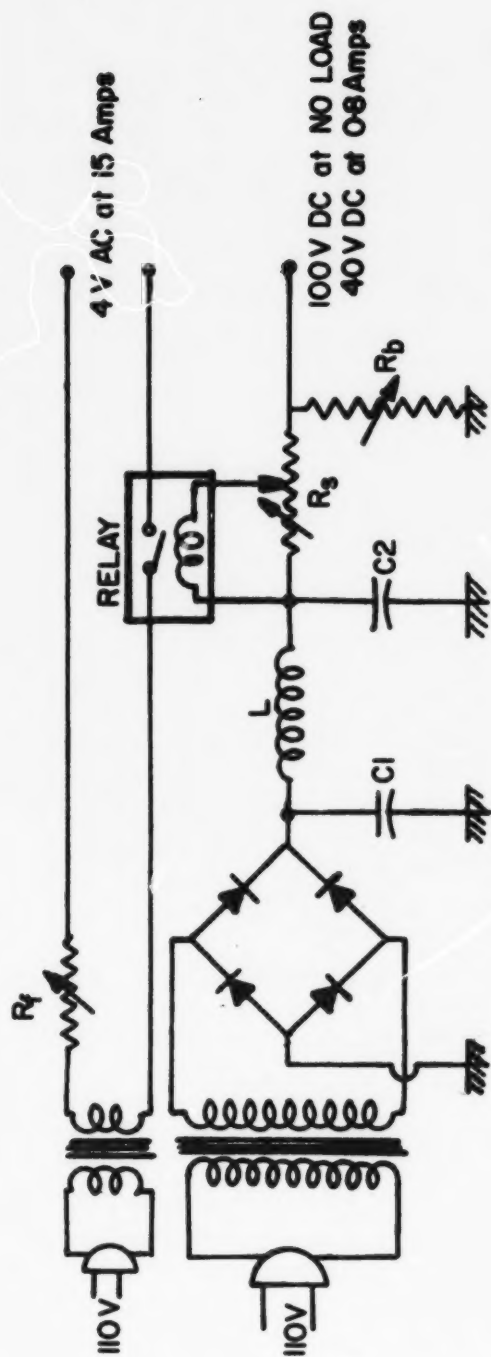


FIGURE D-1



R_1 - Filament Resistor 0-0.5 Ω 45 W
 R_3 - Series Resistor 0-80 Ω 100 W
 R_b - Bleeder Resistor 0-12 K 25 W

C_1 - Capacitor 200 μ F
 C_2 - 100 μ F
 L - INDUCTOR 0.8 Hys

DIODES 200 V PIV
 at 2 Amps
 RELAY 24 V DC

DEUTERIUM ARC LAMP POWER SUPPLY

FIGURE D-2

a relay circuit as shown in figure D.2.

Photomultiplier and Power Supply:

The photomultiplier power supply is regulated by means of 10 OB2 regulator tubes in series. The circuit is shown in figure D.3.

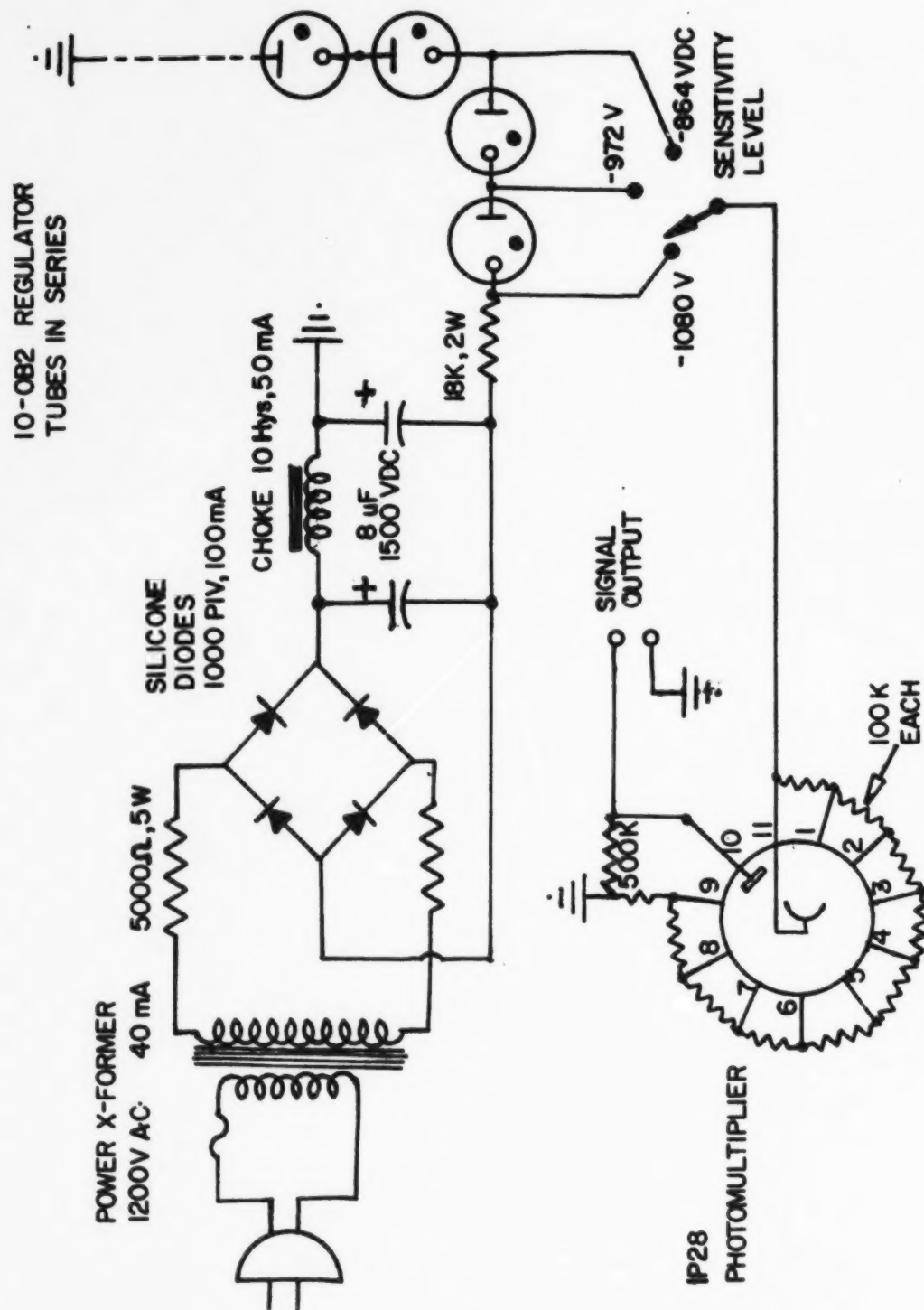
Trigger Pulse Generator:

The sequence of triggering used can be followed in conjunction with figure D.5. The oscilloscope used in this study was a Tektronix, Type 565, Dual-Beam, 4-Channel scope. The two beams can be triggered independently. Further a delayed trigger pulse is available from the back panel of the scope. The delay interval is adjustable.

Beam 1 is triggered by the voltage induced in a coil wound around the ignition coil. The two channels of Beam 1 carry ionisation gap signals and the signals from the trigger pulse generator used to trigger Beam 2.

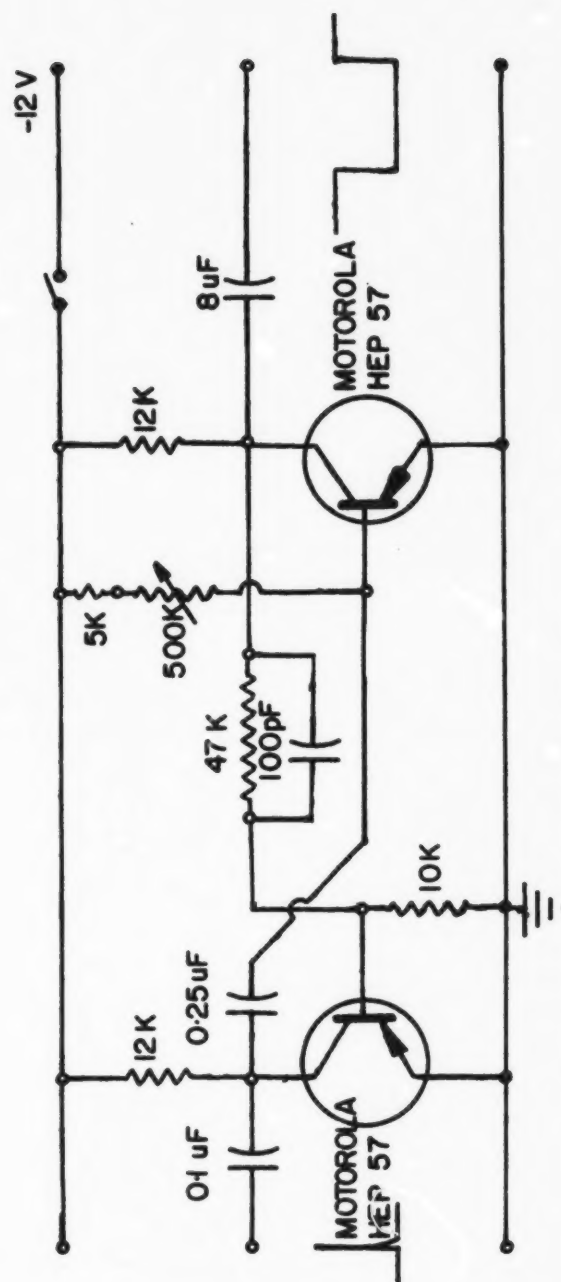
The delayed trigger pulse output from the back panel of the scope is available after an adjustable delay interval after triggering Beam 1 ie after ignition. This pulse provides an input to two monostable multivibrators as shown in figure D.5. The sequence of operation and waveforms can be readily followed from this figure. The metastable period of the multivibrator is adjusted through the adjustable resistor shown in the multivibrator circuit in figure D.4. Thus a series of three trigger pulses is available to trigger Beam 2.

Beam 2 carries the photomultiplier and pressure



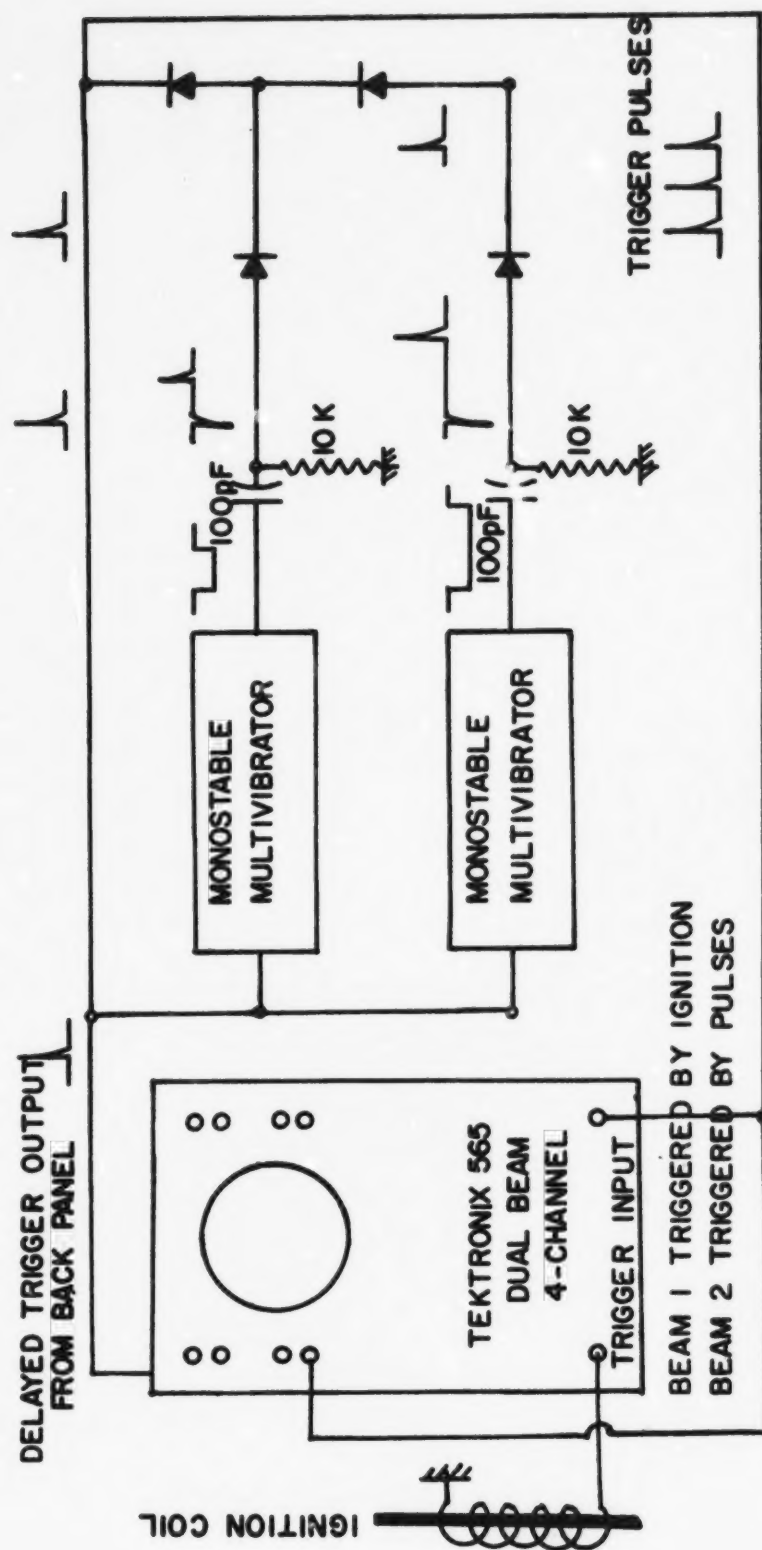
PHOTOMULTIPLIER & POWER SUPPLY CIRCUIT

FIGURE D-3



MONOSTABLE MULTIVIBRATOR

FIGURE D-4

TRIGGER PULSE GENERATORFIGURE D-5

transducer signal. A fast sweep rate can be used on this beam independent of Beam 1. This is desirable in order to obtain better time resolution of measured concentration. Further Beam 2 can be triggered more than once (upto three times) increasing the range of measurement. This is clearly illustrated in figure 3.3 which shows a typical oscilloscope trace. The top two traces are the two channels of Beam 1. Channel 1 carries signals from wall ionisation gaps while channel 2 carries signals from central ionisation gaps, in the same plane as the wall gaps. It can be seen that the flame front arrives at the wall and the centre (in the same plane) simultaneously. It is therefore concluded that the flame is flat. Further channel 2 also carries signals from the trigger pulse generator. This is done through the differential amplifier available on the scope. Trigger pulse signals can be easily distinguished from the ionisation gap signals by their amplitude and rise time. Two of these trigger pulses are used to trigger Beam 2 twice as shown in figure 3.3.

Zero time is fixed by noting the displacement between the first trigger pulse and the window ionisation gap signal. Timing marks based on this zero of time are also shown in figure 3.3.